Synthesis of Polarized Polyenes and Polyenynes.

Structure and Reactivity Studies.

Von der Gemeinsamen Naturwissenschaftlichen Fakultät

der Technischen Universität Carolo-Wilhelmina

zu Braunschweig

zur Erlangung des Grades einer

Doktorin der Naturwissenschaften

(Dr. rer. Nat.)

genehmigte

D i s s e r t a t i o n

Von

Pinar Kiliçkiran

aus Ankara/Türkei

1. Referent: Prof. Dr. H. Hopf
2. Referentin: Prof. Dr. S. Laschat

eingereicht am: 17. 08.2001

Disputation am: 22.10.2001

Abstract

Polyconjugated compounds are attractive systems not only because they are widely found in nature, but also because of their large hyperpolarizabilities. They were found to have potential use as electron relays in chromophores for non linear optics (NLO) or as active components in electronic devices or light emitting diodes. However, the instability and insolubility of polyconjugated systems make it difficult to prepare and investigate them. In the present work the synthesis of several polyconjugated compounds which are terminated by bulky *tert*-butyl groups, that increased both the stability and the solubility of the systems, is reported.

Polykonjugierte Verbindungen sind interessante Systeme, nicht nur weil sie zahlreich in der Natur zu finden sind, sondern auch wegen ihrer sehr großen Hyperpolarisierbarkeit. Sie können als Elektronenrelais in den Chromophoren für die nicht lineare Optik (NLO) dienen, Beiträge in elektronischen Einheiten leisten, aber auch in lichtemittierenden Dioden verwendet werden. Aufgrund der Instabilität und schweren Löslichkeit erweist sich die Herstellung und Untersuchung der polykonjugierten Systeme als äußerst schwierig. In der vorliegenden Arbeit wird die Synthese und Untersuchung von zahlreichen polykonjugierten Verbindungen mit raumerfüllenden tert-Butylendgruppen beschrieben. Die voluminösen Schutzgruppen erhöhen die Stabilität und Löslichkeit dieser Systeme, wodurch strukturelle Untersuchungen ermöglicht werden.

Teilergebnisse aus dieser Arbeit wurden mit Genehmigung der Gemeinsamen Naturwissenschaftlichen Fakultät, vertreten durch den Mentor der Arbeit, in folgendem Beitrag vorab veröffentlicht:

P. Kiliçkiran, H. Hopf, Synthesis of Polyenynes (Poster), *ORCHEM 2000*, 12. Vortragstagung, Bad Nauheim, **2000**.

Die vorliegende Arbeit wurde in der Zeit von April 1998 bis Februar 2001 am Institut für Organische Chemie der Technischen Universität Braunschweig unter der Leitung von Prof. Dr. H. Hopf angefertigt.

I wish to express my sincere gratitude to Prof. Dr. Henning Hopf for his supervision, support and encouragement throughout this research. Without his ideas, remarks, advice and endless interest this study could not have been carried out and completed. The freedom he gave and the joy and satisfaction he shared in each and every single step of this work made it all possible.

I am very grateful to Prof. Dr. Sethuraman Sankararaman and I would like to express my sincere thanks for his advice, valuable discussions and remarks, not only during his short visits to Braunschweig, but from Madras, India also. With his suggestions and comments this study has taken a better shape.

I offer my sincere thanks and appreciation to the members of the Institute of Organic Chemistry, especially to Ms. I. Dix for the X-ray structure analyses; Ms. P. Holba-Schulz for high resolution and 2D NMR spectra; Ms. K. Kadhim and Ms. I. Knust for UV and IR spectra; and Ms. D. Döring, Dr. L. Witte, and Dr. U. Papke for Mass, GC/MS spectra.

I thank all the group members of Prof. Dr. H. Hopf and Dr. U. Jahn for their companionship and friendship. I thank Mr. Z. Hussain for proofreading my thesis and for his suggestions.

I sincerely thank Prof. Dr. S. Laschat for agreeing to be the co-referee of my thesis.

Financial assistance from the Hans Böckler Stiftung, Germany, in the form of a fellowship is gratefully acknowledged.

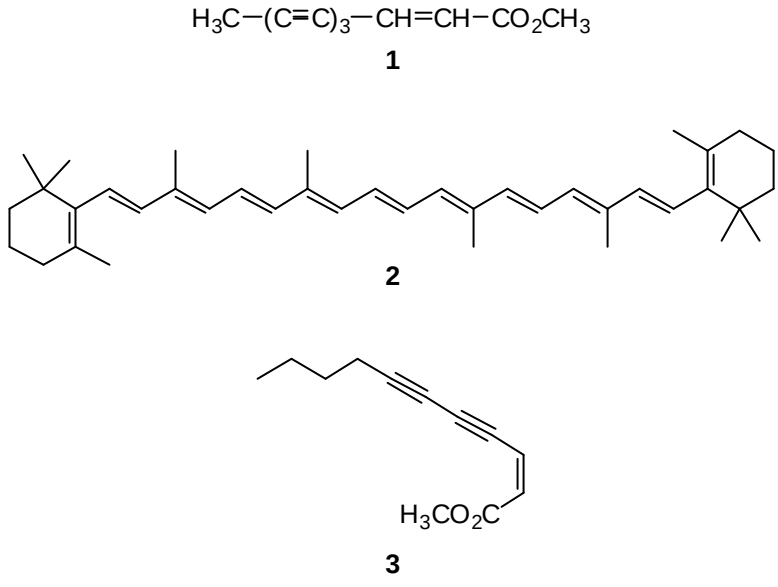
To my sisters

Çigdem & Yasemin

Contents

1. Introduction

If one considers that (a) the first naturally occuring polyacetylene crystals were isolated in 1826, namely that of dehydromatricaria ester **1**[1], (b) the isolation of β-carotene **2**, which has been called the classical compound of polyene chemistry[2], dates back to 1831, (c) the structure of β-carotene was established in 1930[3] (d) the first characterization of a polyacetylenic compound appeared in 1935[1], namely lachnophyllum ester **3**, (e) the total synthesis of β-carotene was first published in 1950[4] and more interestingly also in the March 2001 issue of a chemistry journal[5] (other than dozens of publications over the years[2]), and (f) the Nobel Prize 2000 for chemistry was given to the studies on polyacetylenes[6], it is certainly true that the chemistry of *polyconjugated* compounds is one of the most attractive and intensely researched areas of organic chemistry. Furthermore, more than 600 carotenoids have been isolated from nature from which approximately one third has already been synthesized.[7] The research group of Bohlmann alone has isolated from only two plant families about 700 acetylenes which are mostly polyconjugated.[1]

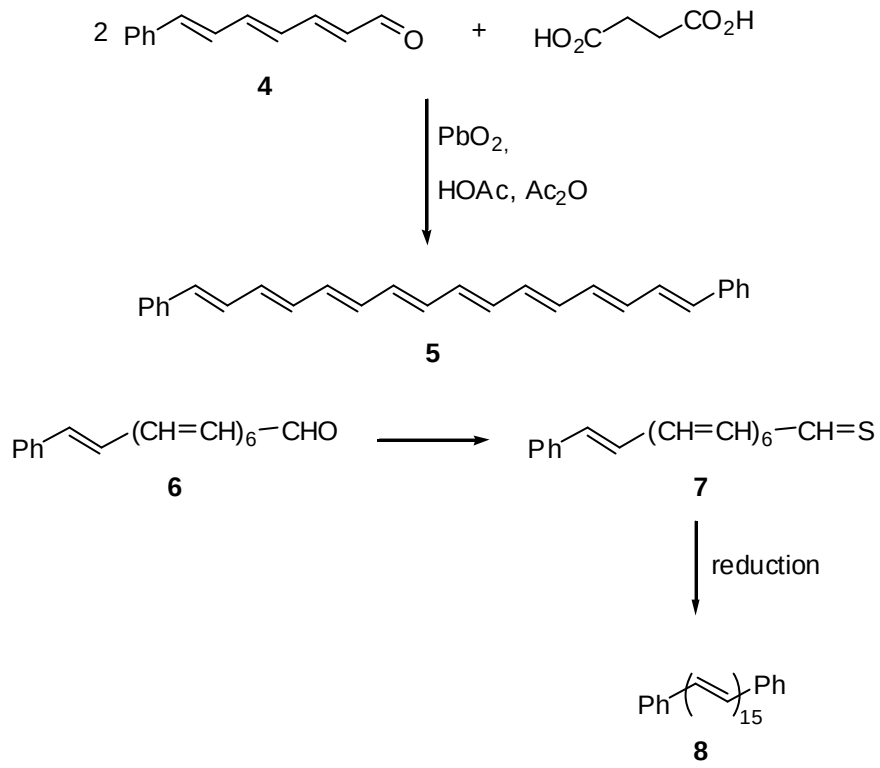


Scheme 1. Earliest examples of polyconjugated compounds isolated from natural sources.

The interest in the isolation and the synthesis of the polyconjugated compounds arose from the curiosity and necessity to learn more about nature (just like any other branch of chemistry and science in general). Although this is still a very important factor, recent and current interest in this area is pointing more and more in the direction of material sciences with the promising results that polyenes can be used as molecular wires in molecular electronics. On the one hand a desire to prepare natural products, not only carotenoids or other terpenes but also polyconjugated bioactive macrolides, or "at least" synthetic systems that can mimic biological oligomers and polymers, and on the other hand the wish to construct ultra-fast, ultra-dense and molecular-sized computational systems,[8] the interest of the researchers on polyconjugated compounds keeps growing and diversifying and will remain like that for many years to come.

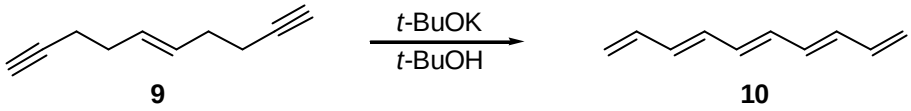
1.1. Polyenes

It is possible to illustrate the most important developments in the synthesis of natural or unnatural polyenes by just looking at the numerous studies published on a single compound which was referred previously as being the classic of its kind, namely β-carotene. However, this would be unjust because we could then overlook the fact that Kuhn had synthesised α,ω-diphenyl subsitituted polyene systems containing up to 15 double bonds in 1937 already. We are yet to match this feat of putting that many double bonds in conjugation using the newest and much more convenient methods of synthesis of olefins presently available. In his approach, Kuhn and his co-workers prepared the α,ω-diphenyl substituted polyenes up to 8 double bonds, **5**, by condensing two molecules of 7-phenyl-hepta-2,4,6-trienal (**4**) with succinic acid in acetic acid - acetic anhydride in the presence of lead oxide. For the synthesis of **8** containing 15 double bonds the necessary aldehyde **6** was first converted into the thio derivative **7** with hydrogen sulfide which then was desulfurized by the use of piperidine or other amines or metals to give the dimerization product **8** (Scheme 2).[9]



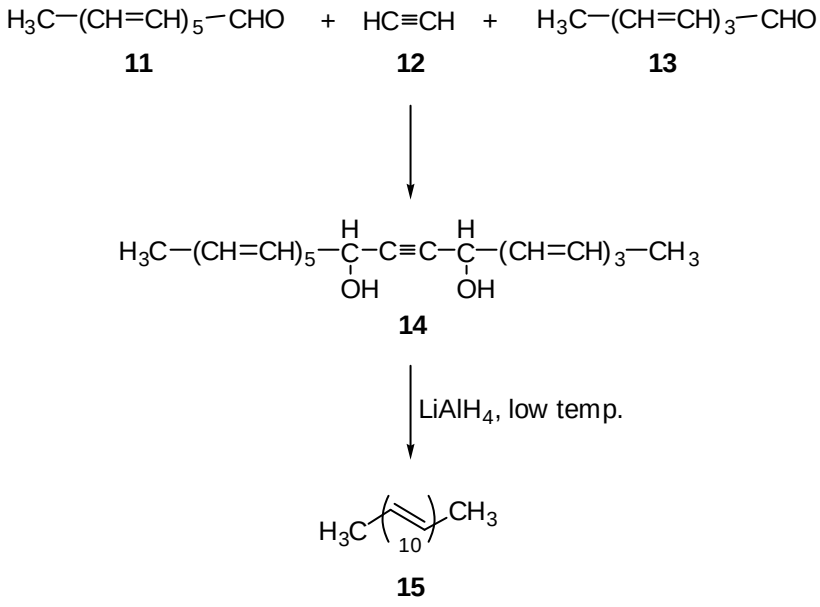
Scheme 2. The synthesis of α,ω-diphenylpolyenes by Kuhn.

The reason of the success in preparing a polyene with 15 consecutive double bonds (despite the inconvenient method) lies in the fact that the polyene chain was "protected" by the terminal phenyl groups. The protection of conjugated molecules with bulky and/or stable terminal groups causes a dramatic increase in their stability. Polyenes that are not protected by bulky groups are very unstable. They oxidize readily in the presence of air, undergo cycloaddition reactions, polymerize very easily and also lose their stereochemical integrity quickly. For these reasons we still do not have much information about the unsubstituted polyenes which contain more then four conjugated double bonds. In 1961 Sondheimer and co-workers reported a method for the synthesis of all-*trans* decapentaene **10**,[10] which they characterized by UV spectroscopic analysis. It was formed in 16% yield and after isolation only 9% survived. In Sondheimer´s route the isomerization of **9** under basic conditions (*t*-BuOK in *t*-BuOH) gave the highly unstable compound **10** (Scheme 3).



Scheme 3. Sondheimer‘ s route to unsubstituted polyenes.

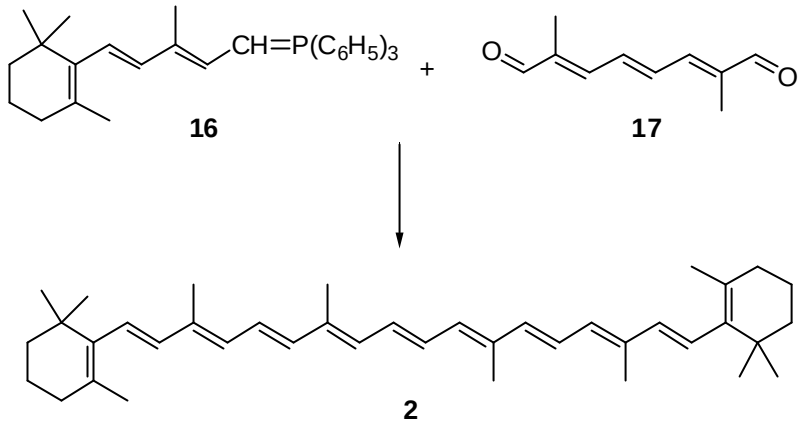
Another early example which showed the increased stability of α,ω-substituted polyenes was provided in 1955 by Whiting and co-workers.[11] The terminal substituents in this case were methyl groups, and the resulting polyenes were still not very stable. However the stabilizing effect of the terminal substitution was obvious, and they managed to prepare α,ω-dimethyl substituted polyenes containing up to 10 double bonds by the reduction of the acetylenic diol **14** with $LiAlH_4$ to the dimethylpolyene **15**. The precursor **14** was prepared by condensation of the unsaturated aldehydes **11** and **13** with acetylene (**12**) (Scheme 4).



Scheme 4. Synthesis of α,ω-dimethylpolyenes by Whiting.

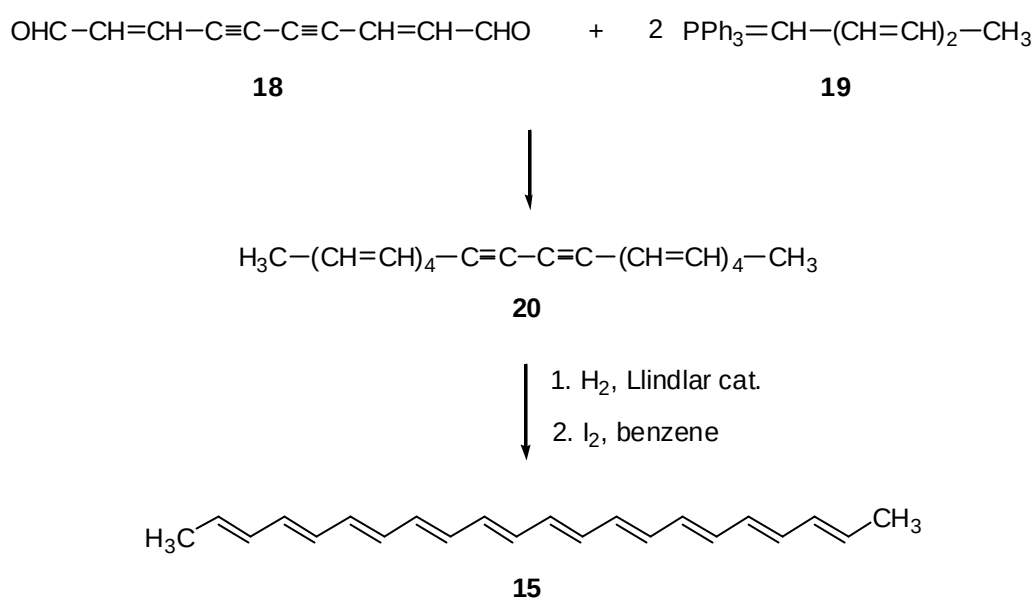
The discovery of the carbon-carbon double bond forming reaction between a carbonyl compound and a phosphorane by Wittig and co-workers in 1953 can definitely be referred as the most important development in the preparation of polyconjugated

compounds.[12] Wittig reported the synthesis of β-carotene **2** in 1956 by using the reaction later named after him. Reaction of 2 equivalents of the phosphorane **16** with the dialdehyde **17** readily gave **2** (Scheme 5).



Scheme 5. Synthesis of β-carotene by the Wittig reaction.

In the same year Bohlmann and his co-workers also used the Wittig reaction for the synthesis of α,ω-dimethyl substituted polyenes.[13] For example the reaction of the dialdehyde **18** with two equivalents of the phosphorus ylid **19** gave the diacetylene **20** which was hydrogenated in the presence of the Lindlar catalyst to the polyene **15** as a mixture of isomers. The isomer mixture was treated with iodine in benzene and the most stable all-*trans* isomer was obtained in good yield (Scheme 6). However, as was mentioned above, although the presence of methyl groups made it possible to prepare these compounds, they were still highly unstable and – furthermore – the typical problem of the insolubility of long chain conjugated compounds had to be faced.



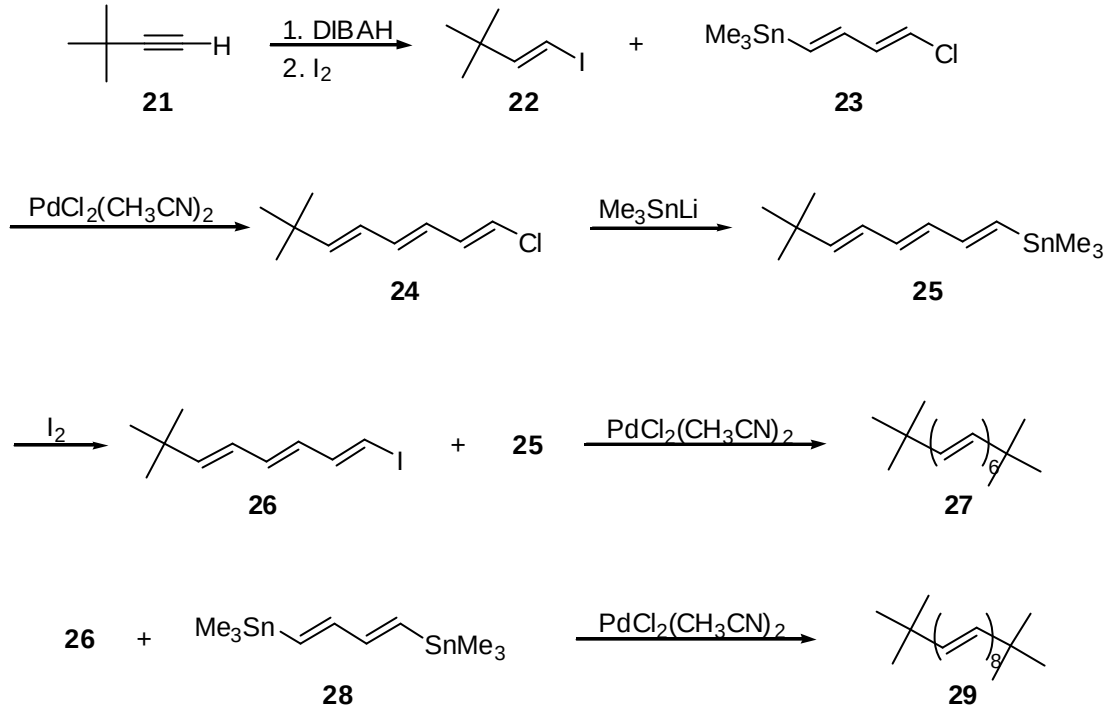
Scheme 6. Synthesis of α,ω-dimethylpolyenes by a Wittig reaction.

The Wittig reaction was used in many other cases for the preparation of long chain polyenes and in the present work it is also the method of choice for the extension of double bonds as discussed in Sec. 2.1.2.a.

Other than the Wittig reaction the most important reactions for formation of C-C double bond, which are also often used in the polyene chemistry, are the Suzuki, Stille, Sonogashira and McMurry type coupling reactions.

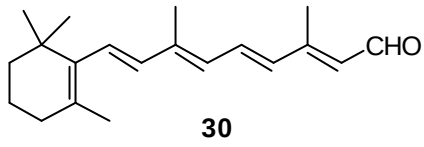
In the preparation of long chain polyene systems with higher stability and solubility Müllen and co-workers have applied the Stille coupling reaction for the preparation of α,ω-di-*tert*-butyl substituted compounds.[14] The first step was the conversion of *tert*-butylacetylene **21** in the presence of DIBAH and iodine to the vinyl iodide **22** which was then coupled with the vinlytin compound **23**, in the presence of $PdCl_2(CH_3CN)_2$, to the chloride **24**. This chloride was converted to **25** which was further used for the preparation of both the iodo compound **26** in the presence of iodine and also as a reagent for the next Stille coupling reaction which gave the di-*tert*-butylsubstituted polyene with 6 double bonds **27**. Coupling between **26** and bis-stannyl derivative **28** was also possible and resulted in compound **29** (Scheme 7). The coupling reactions gave a mixture of *cis* and

trans isomers which were then converted to the most stable all-*trans* isomers by irradiation with light.



Scheme 7. Synthesis of α,ω-di-*tert*-butyl polyenes by Stille coupling according to Müllen.

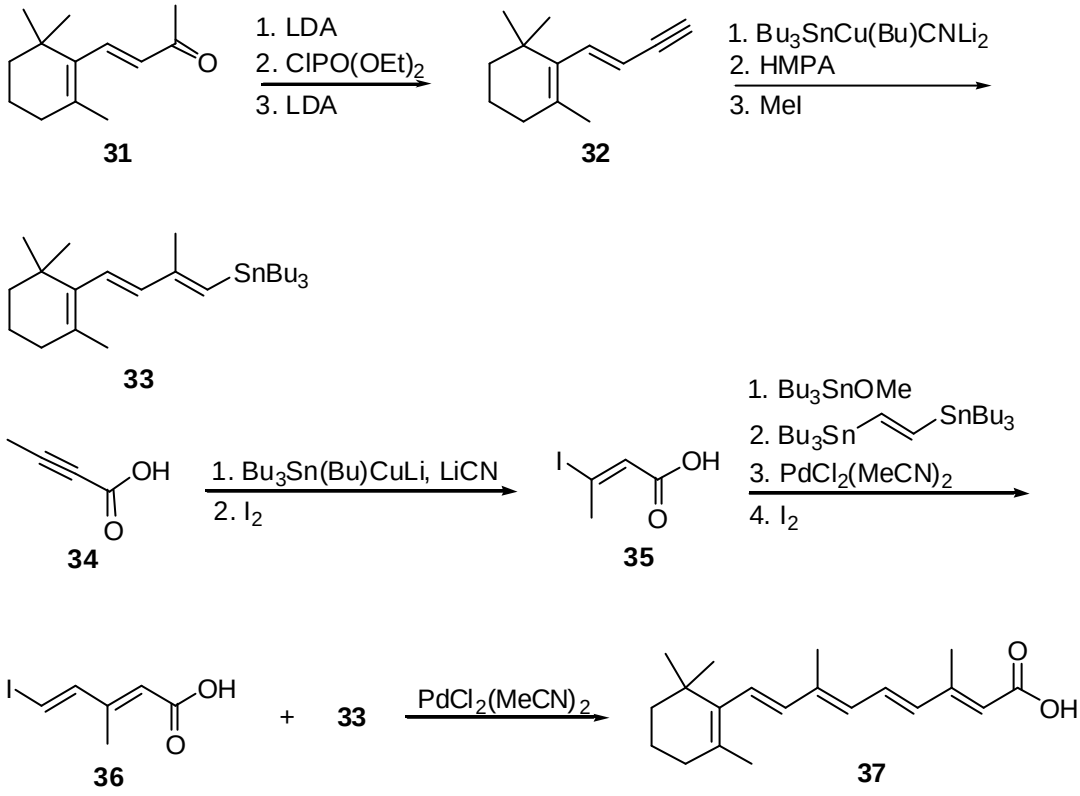
In recent years both the Stille and the Suzuki and Sonogashira coupling reactions have been successfully applied to the preparation of stereochemically pure retinoids which are all derivatives of vitamin A aldehyde (retinal) **30**, which formally can be considered as the half of β-carotene.[2]



Scheme 8. Retinal (vitamin A aldehyde).

An example of the synthesis of all-*trans*-retinoic acid by Stille coupling reaction started with the preparation of dienyne **32** from β-ionone **31** according to the Negishi procedure.[15] Treatment of **32** with 1.1 equivalent of Lipshutz reagent (lithium

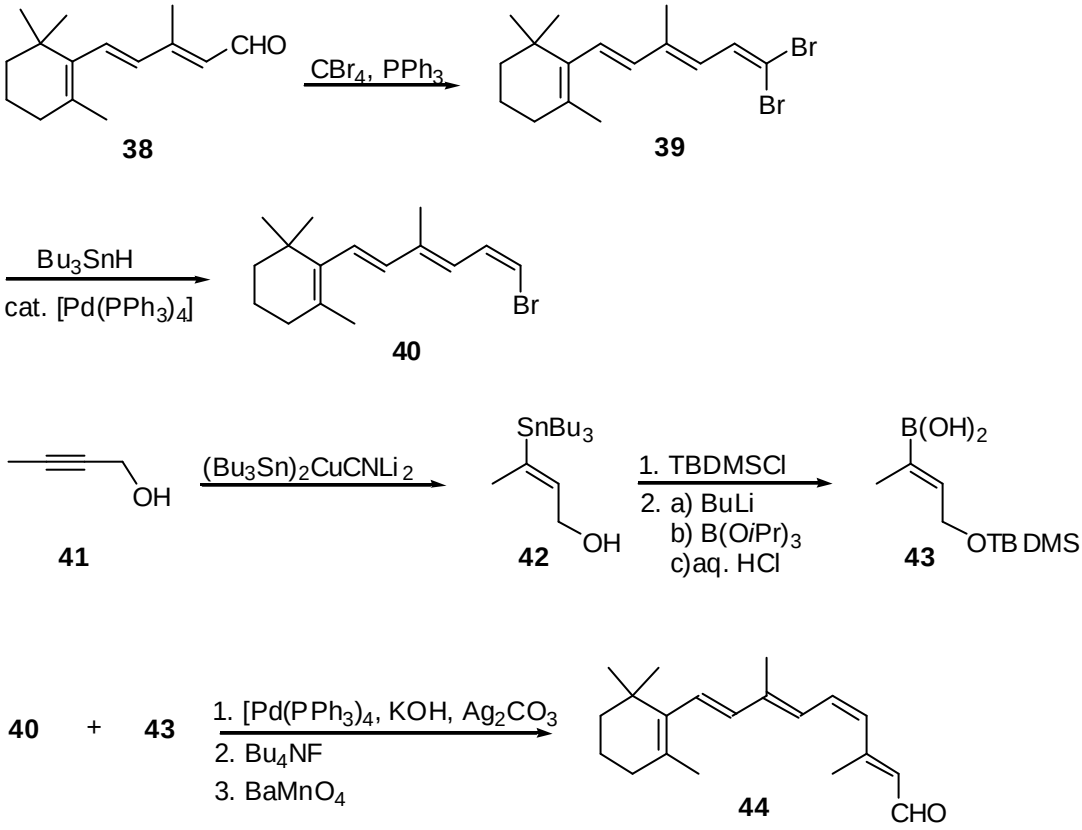
butyltributylstannylcyanocuprate) yielded the intermediate vinylcuprate which was trapped with excess methyl iodide in the presence of HMPA to give the vinylstannane **33**. The synthesis of the other fragment for the final Stille coupling started from tetrolic acid (**34**) which was converted to β-iodovinylic acid (**35**) by stannyl cupration followed by iodine treatment. Coupling of **35** with bis-(tributylstannyl)-ethene in the presence of Pd(II) catalyst stereospecifically provided the corresponding dienyltin compound which was then converted to the iodide **36**. Finally, Stille coupling of **33** and **36** gave all-*trans*-retinoic acid (**38**) in high yield.[16]



Scheme 8. Synthesis of all-*trans*-retinoic acid (**37**) by Stille coupling according to Duchêne.

Two other examples for the synthesis of retinal derivatives, (11*Z*)-retinal **44** and its alkenyl derivative **46** were achieved by Suzuki and Sonogashira coupling reactions starting from the known aldehyde **38**. Dibromomethylation of **38** with carbon tetrabromide and triphenylphosphine gave the compound **39** which was selectively converted to the mono-bromo derivative **40** with tributyltinhydride and catalytic amounts

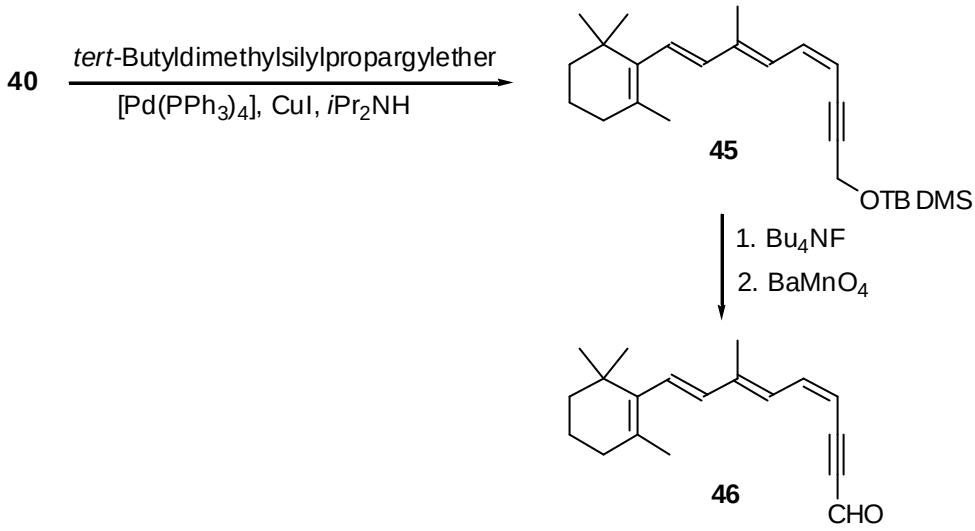
of [$Pd(PPh_3)_4$]. The Suzuki coupling reaction partner **43** was prepared starting from 2-butyn-1-ol (**41**) which was converted to **42** by the regio- and stereoselective addition of tributylstannylcuprate. Protection of the alcohol with *t*-$BuMe_2SiCl$ (TBDMSCl) followed by the substitution of tributylstannyl group with boronic acid gave the compound **43**. The Suzuki coupling of **40** and **43** was performed by using catalytic amounts of [$Pd(PPh_3)_4$], Ag_2CO_3 and aqueous KOH solution. In the final steps the silylether protection was removed by treatment with tetrabutylammonium fluoride followed by the oxidation with $BaMnO_4$ to give the (11-*Z*)-retinal **44**[17] (Scheme 9).



Scheme 9. Synthesis of (11*Z*)-retinal by Suzuki coupling according to Ito.

For the Sonogashira coupling the mono-bromo compound **40** was coupled with *tert*-butyldimethylsilyl propargyl ether in the presence of 5 mol-% [$Pd(PPh_3)_4$], CuI and diisopropyl amine in benzene yielding the protected alkynyl derivative of retinal **45**,

which upon deprotection of TBDMS followed my $BaMnO_4$ oxidation gave the desired compound **46** as single isomer[17] (Scheme 10).

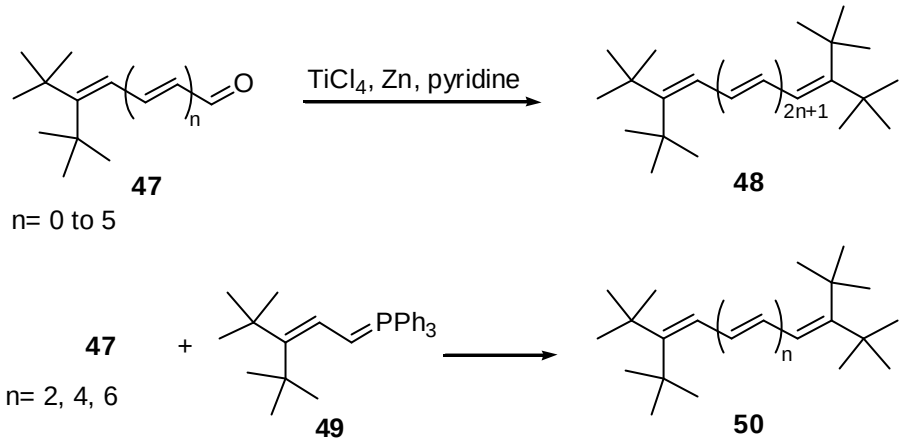


Scheme 10. Synthesis of the retinal derivative **46** by Sonogashira coupling according to Ito.

The high yields and excellent stereoselectivities of both the Suzuki and the Sonogashira coupling reactions are of great advantage in the synthesis of not only retinoids but unnatural polyenes too. Several other examples for the preparation of β-carotene and retinal derivatives using Pd, Zn and Zr catalyzed couplings have been reported in the recent literature.[5, 18-22]

Returning to the unnatural polyenes where the stability problem can be solved by bulky group protection, the poor solubility of the higher polyenes remains as a big problem. A recent and succesfull attempt which is very much related to this work should also be mentioned here. Hopf and co-wokers have reported the synthesis of a series of linearly conjugated, α,ω-tetra-*tert*-butyl polyenes containing up to 13 double bonds using McMurry coupling and Wittig reactions of aldehydes of the type **47** with different chain lengths. The synthesis of di-*tert*-butylaldehydes **47**, not only up to 6 but up to 10 double bonds, is also part of the present work and will be discussed in chapter 2. McMurry coupling of aldehydes **47** using $TiCl_4$, Zn and pyridine gave odd numbered polyenes **48** with very high stereoselectivity and excellent yields, and the Wittig reactions of the aldehydes with the ylid **49** gave the polyenes with an even number of double bonds **50**.

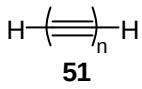
The tetra-*tert*-butyl protection at the termini of the polyenes not only increased the stability but the solubility of these compounds too.[23]



Scheme 11. Synthesis of α,ω-tetra-*tert*-butyl polyenes according to Hopf.

1.2 Polyacetylenes

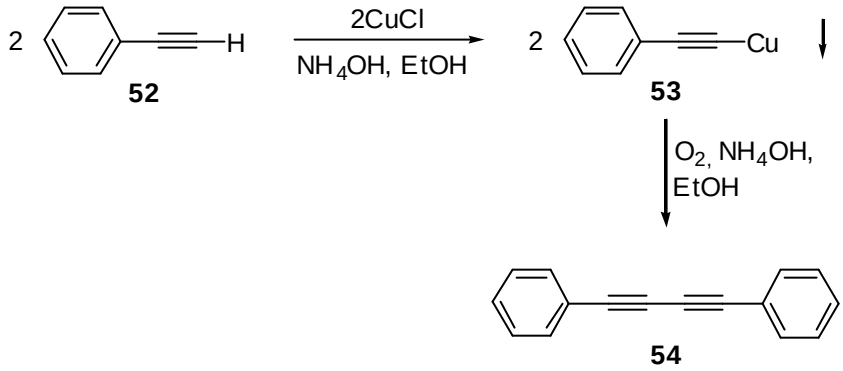
Just like the polyenes most of the polyacetylenes are also highly unstable compounds. This instability is mostly observed in the solid state in which photodecomposition takes place. Bohlmann and co-workers, who obtained hundreds of polyacetylenic compounds from nature and also by chemical synthesis, reported their observations about the photodecomposition as follows; "*Many polyacetylenes exposed to daylight develop quite striking colours. The resulting products, which may be red or blue, are insoluble solids with graphite-like structures*".[1] The instability of the polyacetylenes can again be reduced by the use of bulky terminal groups as in the case of polyenes. The bulky groups hinder the close approach of the polyconjugated chains to each other. However, although the unsubstituted polyacetylenes are still very unstable the situation is much better than in the case of the polyenes. Compounds of the type **51a-j** containing up to 12 conjugated triple bonds with the exception of n = 11 have been prepared and characterized[24] (Scheme 12). Higher homologues beyond triacetylene **51b** are reported to be highly unstable and starting from hexaacetylene **51e** they had been studied only in solution.



51	a	b	c	d	e	f	g	h	i	j
n	2	3	4	5	6	7	8	9	10	12

Scheme 12. Prepared and characterized unsubstituted polyynes.

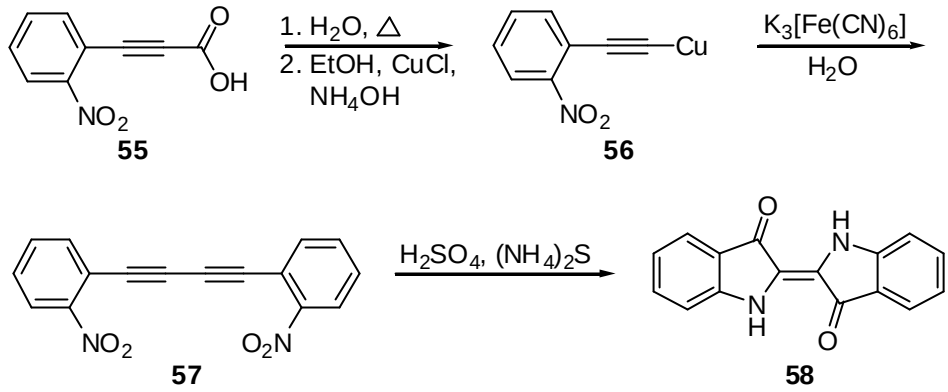
The di- and polyacetylene compounds are mostly synthesised by *sp-sp* carbon coupling processes. The long history of acetylenic coupling dates back to 1869 when Carl Glaser observed that copper(I) phenylacetylide **53** exposed to air underwent oxidative dimerization to diphenyldiacetylene **54** (Scheme 13) .



Scheme 13. First observation of an acetylenic coupling by Glaser.

The reaction starts with the abstraction of the acetylenic proton by the base to form the Cu(I) acetylide which then by intramolecular oxidative coupling of two complexed alkynic groups yields a symmetrical diacetylene.

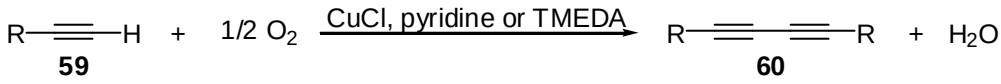
In 1882 Baeyer demonstrated the synthetic utility of this method in his Indigo (**58**) synthesis wherein he also showed that dioxygen itself is not necessary but potassium ferricyanide can also be used as the oxidizing agent[26] (Scheme 14). In 1885 by this modified procedure he prepared the diacetylene **51a** and also its diiodo and dicarboxylic acid derivatives.[27]



Scheme 14. Indigo synthesis by A. v. Baeyer starting from a diacetylene.

In the following years it was shown that other oxidizing agents including cupric salts, potassium permanganate, and peroxides can also be used for acetylenic coupling reactions.

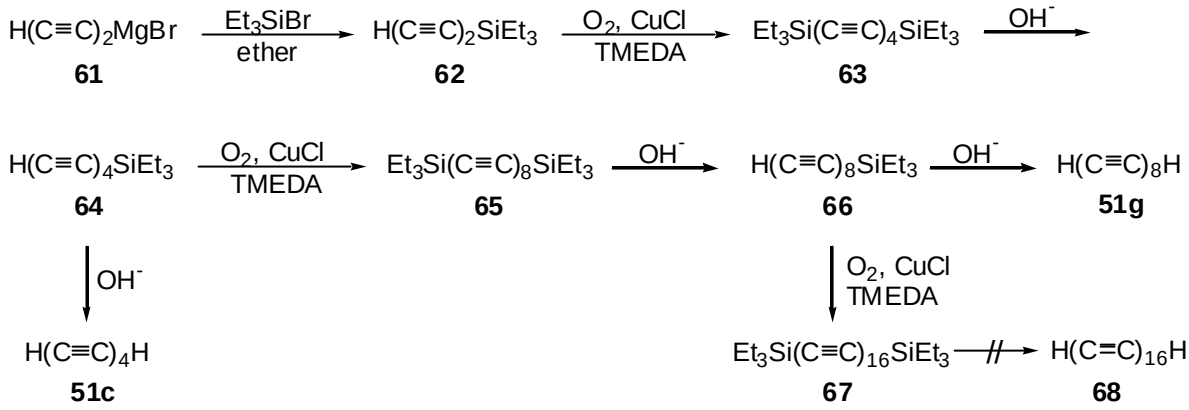
A further and presumably most important modification of the Glaser coupling was reported by Hay and co-workers in 1962.[28] In this approach oxygen gas is passed through a solution of the alkyne and a catalytic amount of Cu(I) salt in a complex forming solvent such as pyridine or *N*,*N*,*N*´,*N*´-tetramethylethylenediamine (TMEDA) (Scheme 15).



Scheme 15. Hay coupling of terminal alkynes.

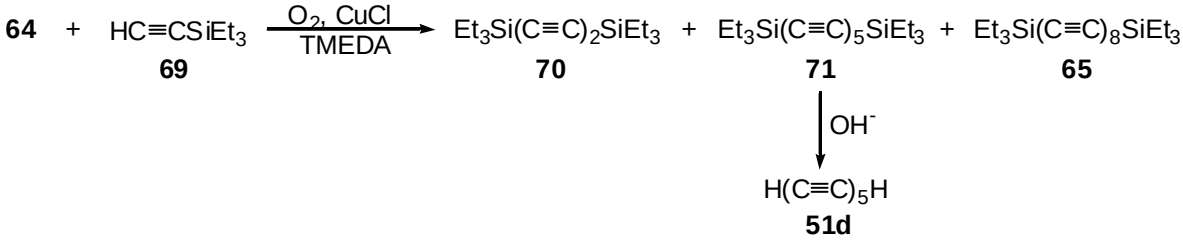
When Glaser coupling or its Hay modification is used for the synthesis of unsubstituted polyacetylenes uncontrolled chain growth occurs because of the high reactivity of the products towards further coupling. However, triethylsilyl protection of the acetylenes has been reported to prevent unwanted chain growth and this protection is also stable under the Hay coupling conditions. Using this approach compounds of type **51** were synthesised. The first step consisted in the conversion of the Grignard reagent **61** to the monoprotected compound **62** by treatment with triethylsilyl bromide. Hay type coupling then gave the bisprotected polyacetylene **63**. Upon treatment with dilute aqueous

methanolic alkali **63** was mono desilylated giving **64** which upon oxidative coupling furnished a bis protected polycetylene **65** again. Complete removal of the silylprotection in **64** gave the desired compound **51c**. Homo coupling reaction of **66** gave **67** with 16 conjugated triple bonds (Scheme 16). Despite the bis protection, the hydrocarbon was highly unstable and it was not possible to obtain it in pure form. This is the longest fully characterized poylacetylene known to date.[2, 24]



Scheme 16. Synthesis of unsubstituted polyacetylenes by Hay type coupling.

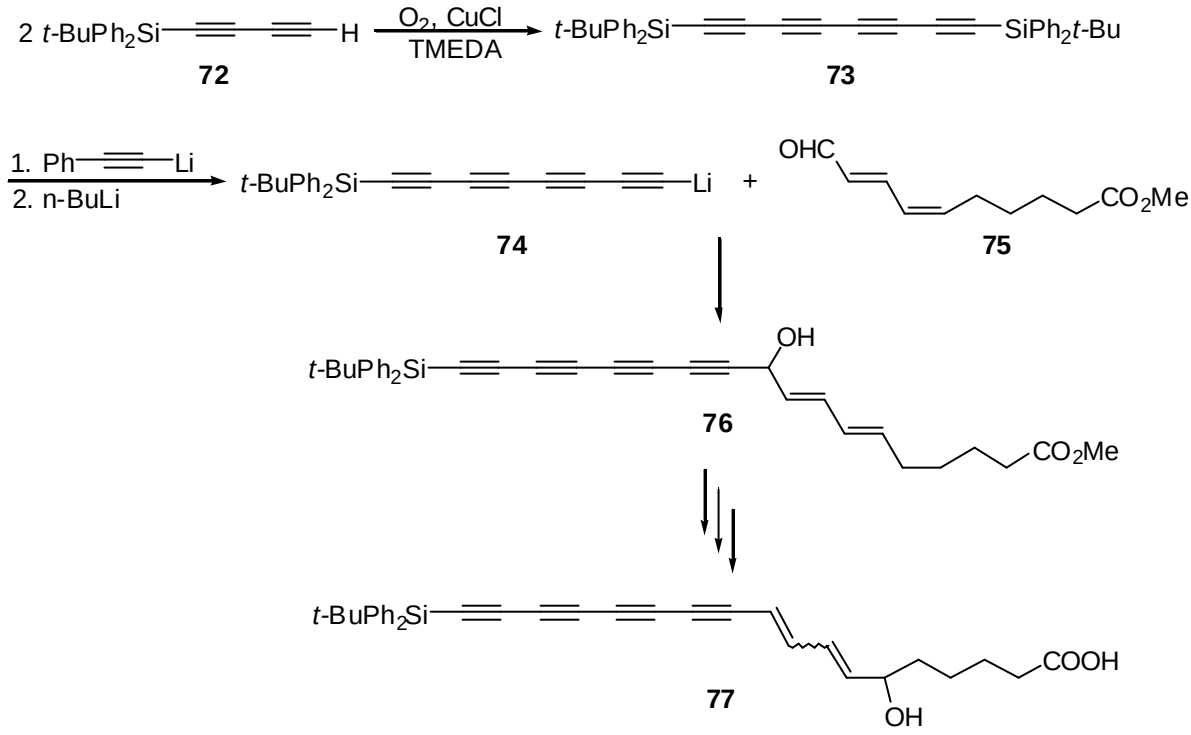
By the same method mixed coupling reactions can also be performed to obtain an odd number of triple bonds, however, as can be expected, formation of three different coupling products cannot be prevented (Scheme 17).



Scheme 17. Preparation of unsubstituted polyacetylenes with odd number of triple bonds.

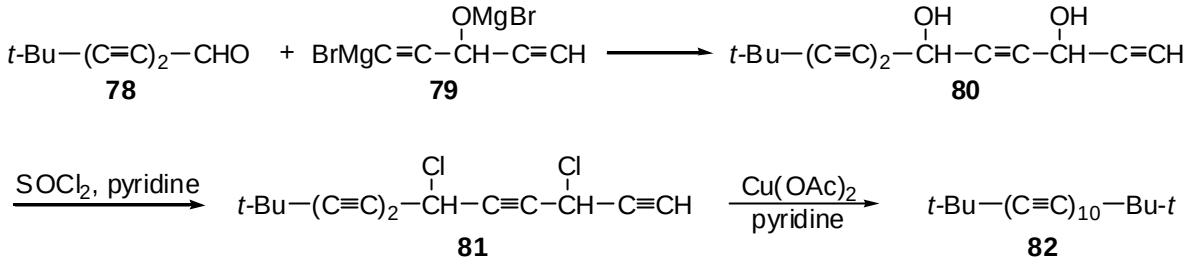
A nice example of a Hay type coupling of silyl protected acetylenes with a selective deprotection has been reported by Yamaguchi and co-workers.[29] They used the acetylene coupling reaction in the total synthesis of caryoynencins **77** which are polyyne

antibiotics. The monosilyl protected diacetylene **72** was subjected to oxidative homocoupling in the presence of CuCl in TMEDA. The di-silyl protected tetrayne **73** was then mono-deprotected carefully by phenylethynyl lithium followed by the subsequent addition of *n*-BuLi to give the lithium acetylide **74**. Reaction of **74** with the aldehyde **75** gave **76** which was further converted to the target molecule **77** (Scheme 18).



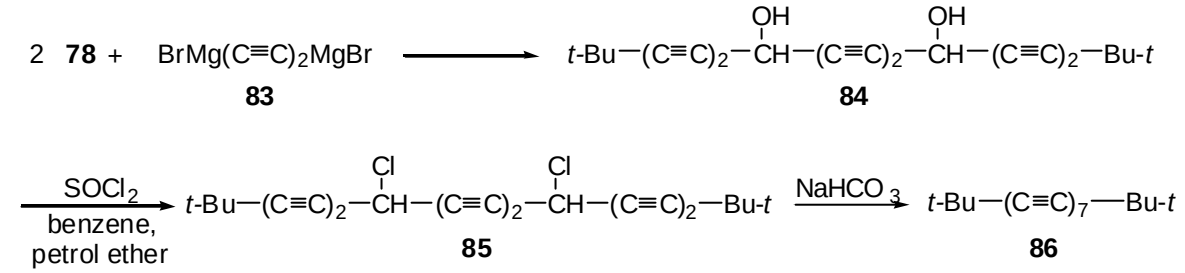
Scheme 18. Acetylenic coupling in the total synthesis of caryoynencins.

The coupling reaction by copper(II) acetate in pyridine is also a useful procedure and mostly referred as the Eglinton method.[30] It is also quite often used for making cyclic alkynes. An important example of the Eglinton reaction in the synthesis of linearly conjugated all-carbon chains has been reported by Jones and co-workers.[31] The polyyne systems were stabilized by *tert*-butyl protection. Reaction of the diacetylenic aldehyde **78** with the Grignard reagent **79** gave the diol **80** which was then converted to its dichloride **81** by reaction with thionylchloride. Treatment of **81** with $Cu(OAc)_2$ in pyridine finally gave the polyacetylene **82** (Scheme 19).



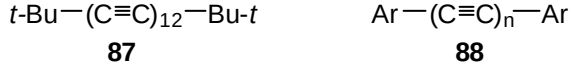
Scheme 19. Synthesis of di-*tert*-butyl protected polyacetylenes by Jones.

Seven years before the report of Jones and co-workers, Bohlmann was able to synthesise the *tert*-butyl protected chain with 7 conjugated triple bonds by a bis Grignard reaction. He prepared the polyacetylene **86** by reacting two equivalents of the acetylenic aldehyde **78** with the bis Grignard reagent **83**. The alcohol **84** thus formed was converted to its dichloride **85** which on dehydrochlorination using sodium bicarbonate gave compound **86**[32] (Scheme 20).



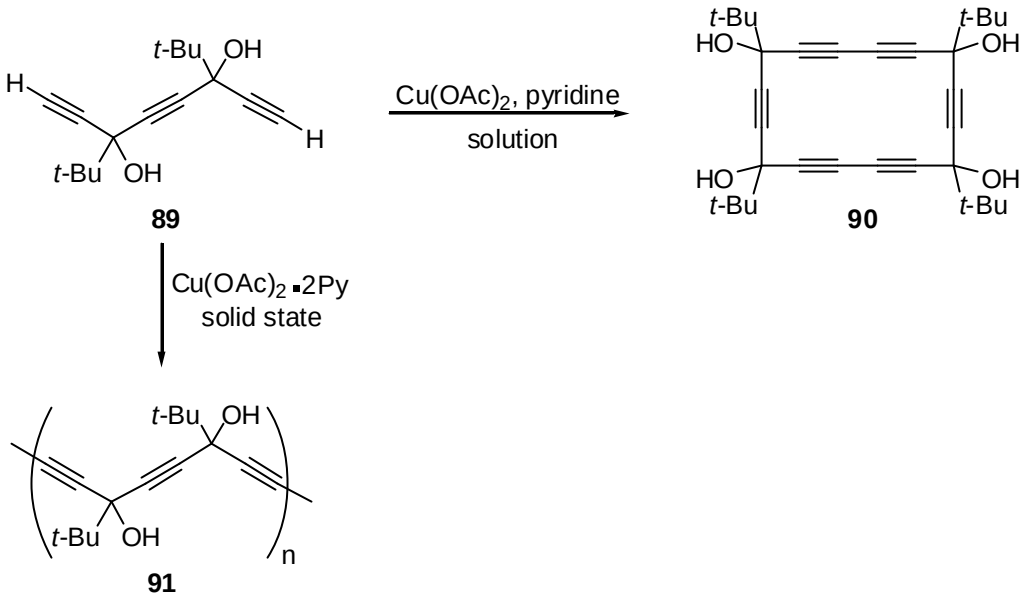
Scheme 20. Preparation of di-*tert*-butyl protected polyacetylenes by Bohlmann.

Compound **87** (the longest member of its series)[33] and several aryl-substituted polyacetylenes[2, 34] **88** were synthesised by the above oxidative homocoupling methods (Scheme 21).



Scheme 21. More linear conjugated polyacetylenes.

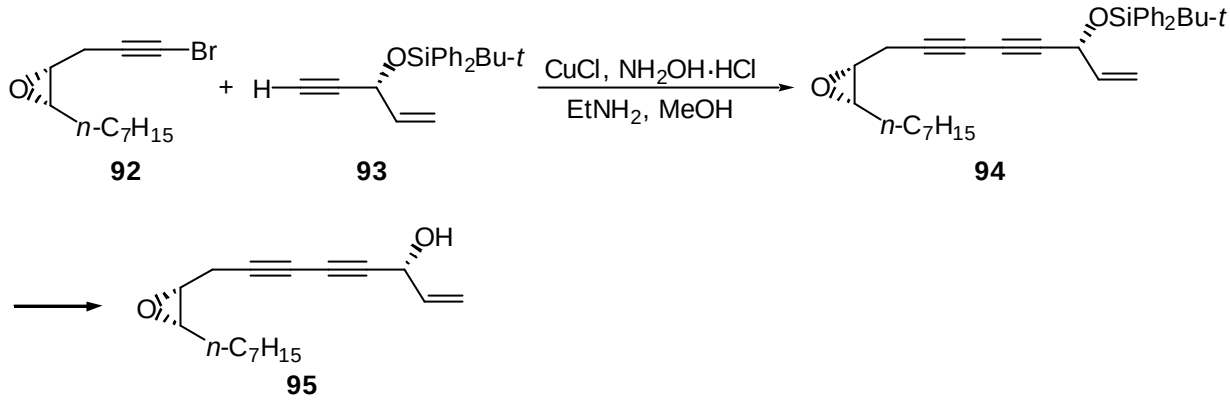
In this context it is important to mention that oxidative coupling reactions are not only limited to the liquid phase but reactions in the solid state have also been reported. An interesting example employing Eglinton conditions is the formation of compounds **90** and **91**. The coupling of **89** in pyridine using $Cu(OAc)_2$ gave the cyclic dimer **90**, whereas the solid state reaction using $Cu(OAc)_2 \cdot 2py$ yielded the linear coupling product **91**[35] (Scheme 22).



Scheme 22. Oxidative coupling reactions in solution and solid state.

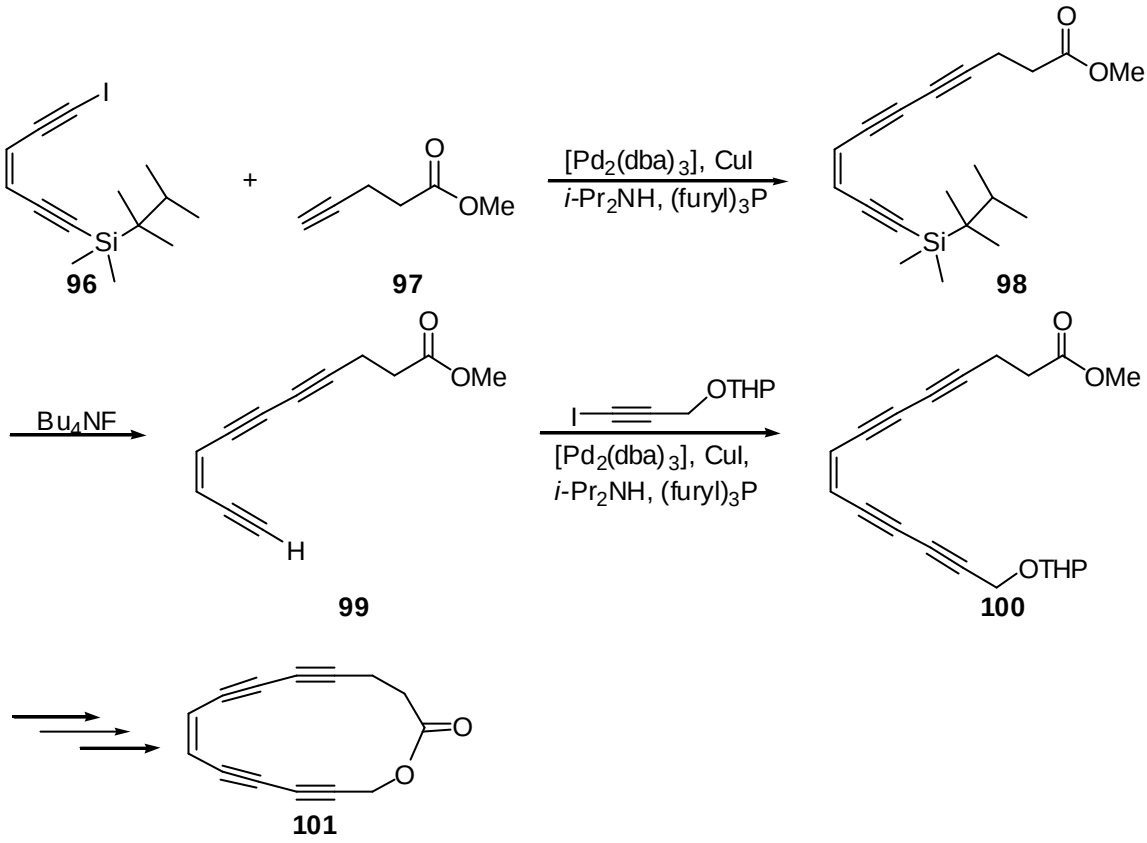
The oxidative coupling reactions mentioned so far are all very useful for the preparation of symmetrical polyacetylenes. However, as can be expected, they are quite unsatisfactory for heterocoupling reactions because of the simultaneous formation of a mixture of symmetrical and unsymmetrical products. A very useful and an important method for heterocoupling is the so-called Cadiot-Chodkiewicz reaction. It is the reaction between a terminal alkyne with a 1-bromoacetylene in the presence of copper(I) salt and a suitable amine. Because this method tolerates numerous functionalized starting materials including alcohols, polyols, quinols, epoxides, peroxy substituents, amines, acetals, carboxylates, carboxylic esters, amides, disulfides, acetylenic silyl-protecting groups and nitroxy radicals, it has found broad application for the synthesis of many polyunsaturated systems.[36]

A recent example showing the importance of Cadiot-Chodkiewicz reaction in the synthesis of natural acetylenes has been reported by Cai and co-workers.[37] They prepared the carbon skeleton **94** of the antitumor agent panaxydol **95** from the reaction of bromoacetylene **92** with the terminal acetylene **93** using CuCl, $NH_2OH{\cdot}HCl$ and ethylamine in methanol (Scheme 23).



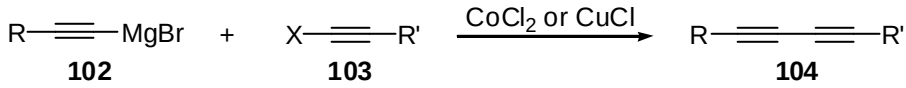
Scheme 23. Cadiot-Chodkiewicz reaction in the carbon frame work preparation of Panaxydol.

Pd catalyzed cross coupling reactions are also very often used and have been reported to be superior to the Cadiot-Chodkiewicz reaction especially in the preparation of *cis*-enediyne and *cis*-enetetrayne systems. *Cis*-enediynes have received great interest in the recent years as potential anti-tumor antibiotics.[38] Macrocyclic enetetrayne **101** which was prepared by Schreiber and co-workers is an example of Pd catalyzed alkyne cross-coupling reaction[39] (Scheme 24).



Scheme 24. Synthesis of a macrocyclic enetetrayne by Pd catalyzed coupling reaction.

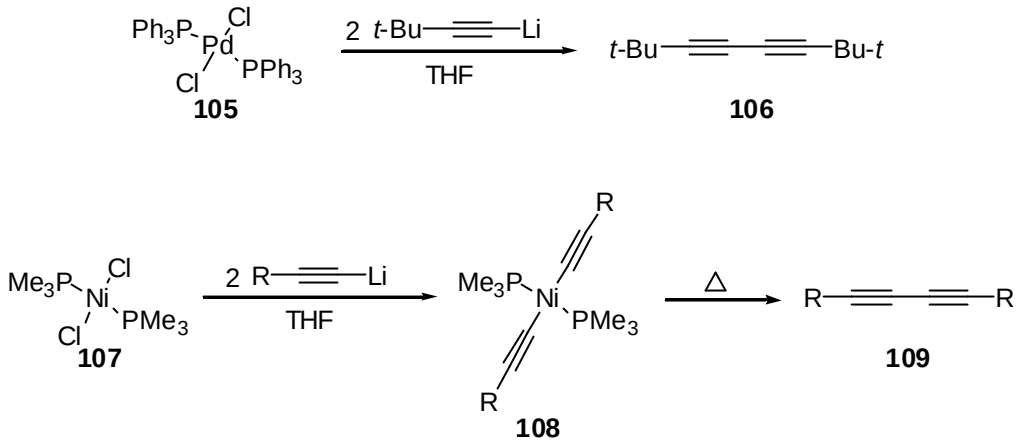
A variation of the Cadiot-Chodkiewicz reaction is provided by the coupling between alkyne Grignard derivatives and 1-haloalkynes. Copper(I) and cobalt(II) salts are commonly used as catalysts here (Scheme 25). But the reaction did not find wide use so far because of homocoupling arising from halogen-magnesium exchange.



Scheme 25. Alkyne Grignard and 1-haloalkyne coupling reaction.

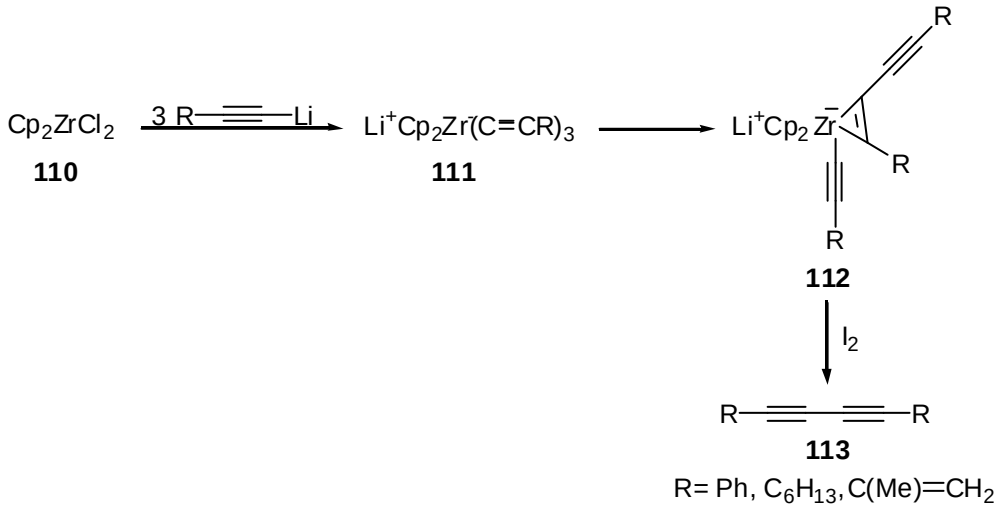
Several other organometallic acetylides have been reported as alternatives to the magnesium acetylides. Lithium acetylides are most widely preferred. For the preparation of homocoupled products a large variety of oxidizing agents has been reported to be

effective. Another strategy involves the addition of lithium acetylides to nickel or palladium complexes (Scheme 26).



Scheme 26. Coupling of alkynyl lithium derivatives using Pd and Ni complexes.

Lithium acetylides are also often used as precursors for transmetallations which yield metalated alkynes. These alkynes then participate in coupling reactions giving the dimerized products. Boron, tin, antimony, selenium, tellurium and nickel are reported to be quite effective[40]. An example involving alkynyl zirconecenes, reported by Negishi and co-workers, is given below[40] (Scheme 27).



Scheme 27. Synthesis of symmetrical diynes by 1,2-migration reaction of alkynylzirconecenes.

There are many other methods available for both homo- and heterocoupling reactions of alkynes. However none of them has been so effectively used as the classical Glaser process. In the present work the Hay type modification of Glaser coupling is used for the preparation of tetra-*tert*-butyl protected polyenediyne and polyenetetrayne compounds which will be discussed in Sec. 2.5.4.

In the last century many natural products with di- or polyacetylenic moieties have been prepared, numerous unnatural cyclic or acyclic polyacetylenes have been reported, and the synthesis of acetylenic carbon allotropes made its strong impact on organic chemistry and material science. The resulting products have been investigated or are still under investigation either to understand more about nature or to find compounds with novel electronic and optical properties. But unfortunately the reactions themselves have not been investigated as much as the products they give. The mechanism of more than a 100 years old classical oxidative alkyne couplings still remains unknown!

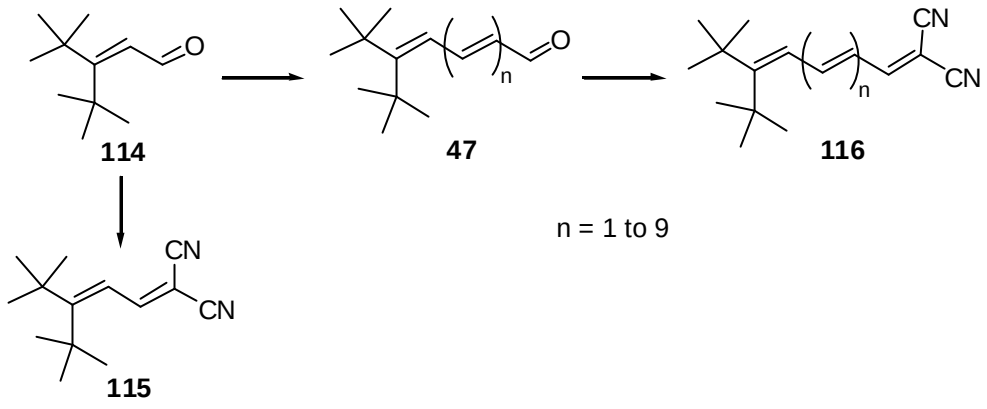
1.3. Aim of the work

Since the discovery of the outstanding role of polyacetylene as a conducting polymer[41] the electronic properties of linear π-conjugated systems have attracted considerable attention. Long conjugated chain molecules are interesting systems because of their possibilities of having very large hyperpolarizabilities. They were found to have potential use as electron relays in chromophores for non linear optics (NLO) or as active components in electronic devices or light emitting diodes.[42] Most of the electronic properties of linearly conjugated systems are directly related to the HOMO and LUMO levels and to the width of the HOMO-LUMO gap. That is why optimal π-electron delocalization is a crucial point in the design of systems that may serve as NLO materials or molecular wires.

In the first two sections of this chapter methods for the synthesis of polyconjugated molecules were explained briefly, and it was also mentioned, that to achieve stable longer systems requires bulky group protection. In the present work several di- and tetra-*tert*-butyl protected polarized polyenes and tetra-*tert*-butly protected polyenynes were synthesized which are expected to have interesting electronic and structural properties.

1.3.a. Dicyano functionalized polyenes

A linear cyano group which has a cylindrical π-cloud is always in conjugation with an attached π-system and has a strong electron withdrawing power with a small steric bulk.
It has been reported that the introduction of cyano groups at the terminal positions of conjugated chains results in the increase of the NLO properties of the systems.[43, 44, 45] It is also known that cyano group substituted systems show extreme bathocromic shifts which could be of use in the application of these systems as dye stuffs. The first part of this work includes the synthesis and structural investigations of a series of α-dicyano substituted polyenes which are stabilized by di-*tert*-butyl groups at the ω-postions **115**, **116**. The synthetic route started with the aldehyde **114**[46] which by Wittig or Horner-Emmons type reactions increased in chain length up to 10 double bonds **47**. The di-cyano groups were introduced by a Knoevenagel type condensation reaction of the aldehydes with malononitrile (Scheme 28).



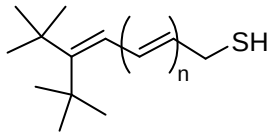
Scheme 28. Synthetic route to the dicyano functionalized polyenes.

1.3.b. Thio-group functionalized polyenes

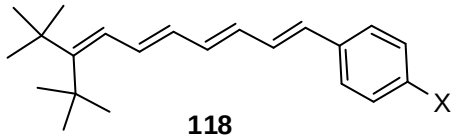
The formation of oriented monolayer films on a metal surface by the spontaneous adsorption of molecules from solution is known as self-assembly. Of all known types of self-assembled monolayers (SAMs) two systems have shown great promise as a means of

controlling the chemical structure of organic surfaces, a) adsorption of organosulfur compounds on noble metals such as gold and silver, b) reaction of alkyl-trichlorosilanes with silicon or glass. It is of interest to attach electrochemically reactive molecules to metal surfaces because first of all the intramolecular and electrochemical electron transfers could be investigated, and secondly the chemical and optical properties could be exploited.[47, 48]

The studies on SAMs that are prepared by adsorbing thio-functionalized conjugated molecules on gold surface are reported to give promising results. Such systems are expected to have potential use as switching elements in future computational systems.[49 - 51] However, probably because the linearly conjugated polyene systems are highly unstable, SAMs prepared from thio-terminated linear polyenes are not reported to date. The second part of the present work includes the synthesis of thio-group attached polyene systems of the type **117** and **118** which are stabilized by di-*tert*-butyl groups at one terminus. Compounds of type **117** were prepared from the reaction of chlorides with thiourea. And compounds **118** were prepared by the Wittig reaction of the appropriate aldehyde with the necessary *para* substituted benzylic Wittig salts (Scheme 29).



117 n = 0, 3



118

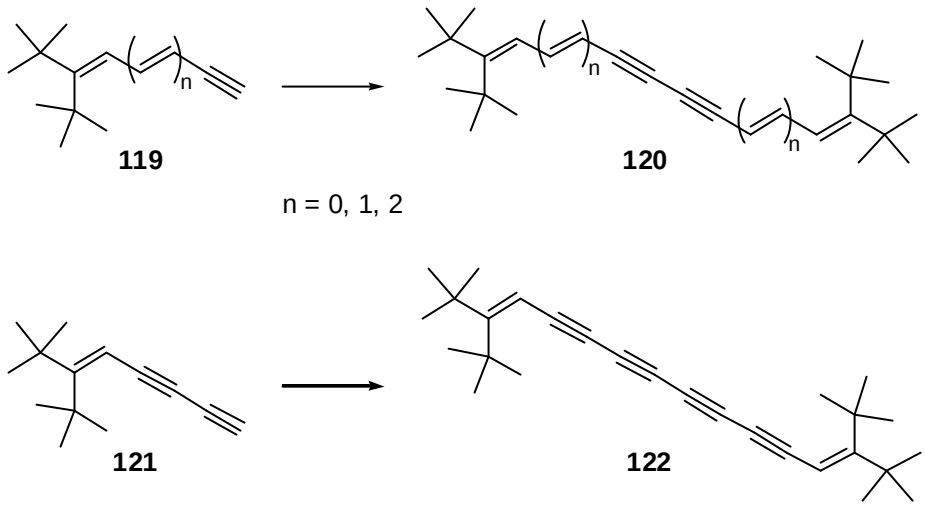
X = SCH_3, $SOCH_3$, SO_2CH_3, SH

Scheme 29. Thio group functionalized polyenes.

1.3.c. Polyenynes

The third part of this work consists in the synthesis and structural investigations of α,ω-tetra-*tert*-butyl protected polyenediyne and polyentetrayne systems. In this context

terminal acetylenes of type **119** and **121** were prepared which were then converted to the target molecules **120** and **122** by oxidative coupling reactions (Scheme 30). The instability problems of polyacetylenes, especially in the crystalline state were mentioned before. Here it was aimed to show that this problem could be overcome by bulky group protection which will allow complete structural analysis that brings a much deeper understanding of analogous systems. Compounds **120** and **122** were also investigated in view of their reactivities towards the conversion into thiophene derivatives, the fourth and last aim of this study.

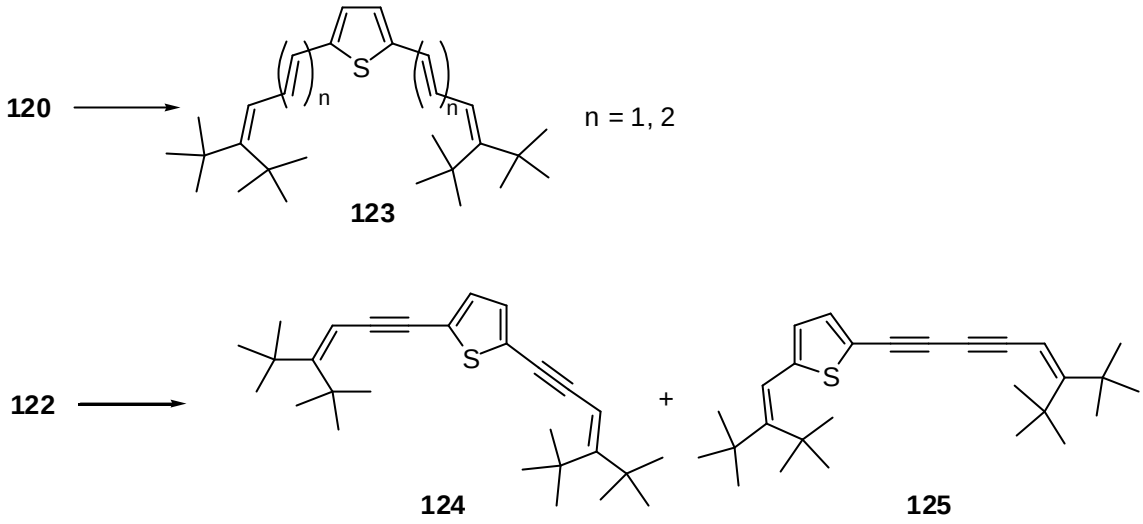


Scheme 30. *tert*-Butyl stabilized polyenynes.

1.3.d Polyconjugated systems with thiophene units

Recently it was shown that thiophene bearing polyconjugated systems are potential canditates as NLO materials. Employing a thiophene ring as a conjugating unit in a chain results in very large nonlinearities. Also enhanced photoluminescence properties of conjugated systems can be achieved by the presence of thiophene units, making them very important materials for light-emmiting devices.[8, 52, 53, 54] A very important reaction in the field of natural acetylenes is the thiophene formation by the addition of H_2S to the conjugated triple bonds. Using nature as a model the polyenediyne and poylenetetrayne systems **120**, **122** were converted to the thiophene derivatives **123** - **125**, in the last part of

this work (Scheme 31). The aim was to show a route for the preparation of tetra-*tert*-butyl stabilized thiophene containing conjugated systems and to investigate them structurally.



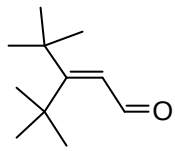
Scheme 31. Thiophene derivatives.

2. Results and discussion

2.1. Synthesis of polyene aldehydes

2. 1. 1. Synthesis of 3-(*tert*-butyl)-4,4-dimethyl-2-pentenal (114)

As mentioned in the previous chapter the stabiltity of polyconjugated compounds is increased strongly by the use of bulky terminal groups and throughout this work *tert*-butyl groups are used for terminating/protecting both the polar polyenes and the polyenynes. A suitable starting material for this purpose should contain the *tert*-butyl groups from the very beginning. It was also necessary to have a functional group which could easily be used for further chain extensions and also for the transformation to other functionalities. The known aldehyde **114**[46] can be considered as the starting material and the key compound through out this work. (Scheme 32)

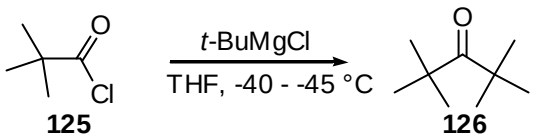


114

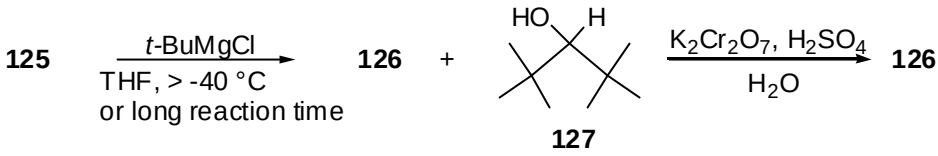
Scheme 32. 3-(*tert*-Butyl)-4,4-dimethyl-2-pentenal, starting material of the present work.

The route for the sythesis of the aldehyde **114** started with a Grignard type reaction between *tert*-butyl acetylchloride **125** and *tert*-butylmagnesiumchloride in anhydrous THF at -45 - -40 °C which gave the di-*tert*-butyl ketone **126** in 80% yield (Exp. 4.3.1). When the reaction was carried out below −45 °C the yields were much lower. At a lower temperature the reaction is not taking place to completion so letting the reaction mixture warm up to room temperature causes the unreacted material to react very exothermically (starting around −30 °C), which may cause uncontrollable warming up resulting in explosions! For a satisfactory yield the reaction has to be carried out with freshly prepared *tert*-butylmagnesiumchloride and should be worked up on the same day. A reaction temperature above −40 °C and also letting the reaction mixture stay overnight

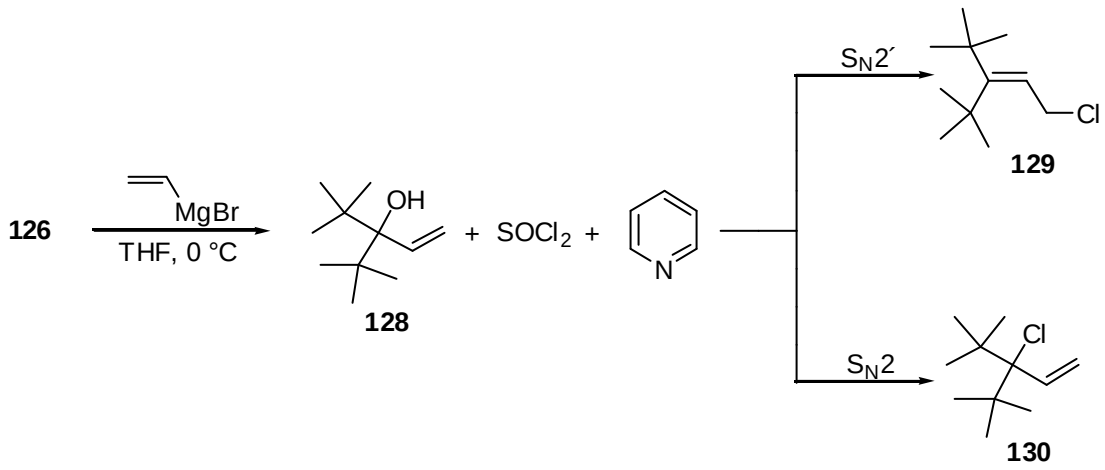
was observed to cause formation of a side product, alcohol **127**, which could be converted to the desired ketone by a subsequent oxidation reaction with $K_2Cr_2O_7/H_2SO_4$. Altough the oxidation of the alcohol to the ketone proceeds in 100% yield the time and material lost for this undesired reaction should be considered and it hence be prevented.



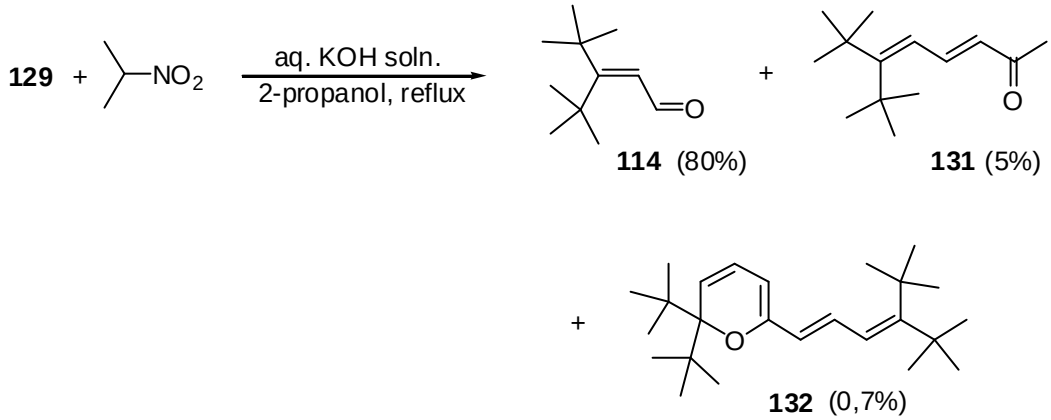
125 **126**



In the next step **126** was converted to the allyl alcohol **128**, again with a Grignard reaction, now with vinylmagnesiumbromide in anhydrous THF at 0 °C (Exp. 4.3.2). This reaction should be carried out in a large amount of solvent otherwise at 0 °C, during the addition of the Grignard reagent, the mixture solidifies inhibiting the process causing very low yields. The alcohol **128** was then converted to a vinylic chloride **129** by $SOCl_2$ and pyridine in diethylether (Exp. 4.3.3), a reaction very likely taking place according to a S_N2' mechanism.[55] The competing S_N2 reaction could not be prevented fully causing the yield of the desired product **129** to remain around 60 %. Carrying the reaction above 0 °C gave the allylic chloride **130** as the major product (54%).



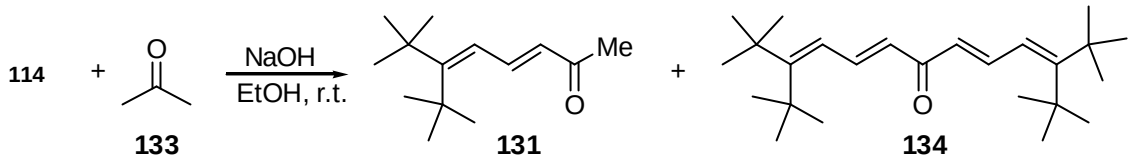
For the synthesis of the aldehyde **114**, the last step, a Hass-Bender reaction[56] was used, in which **129** was reacted with freshly distilled 2-nitroporpane and aq. KOH solution in 2-propanol under reflux (Exp. 4.3.4). Although **114** has been prepared by the same method for several years in our laboratories the formation of two additional products has been overlooked. Besides the aldehyde **114** formed in 80% yield, two further products, namely, 6-*tert*-Butyl-7,7-dimethyl-octa-3,5-dien-2-one (**131**) in 5% and 2,2-di-*tert*-butyl-6-(4-*tert*-butyl-5,5-dimethyl-hexa-1,3-dienyl)-2H-pyran (**132**) in 0.7% yield are generated. The formation of these side products will be discussed on the following pages (Sec. 2.1.1.a). The aldehyde **114** was further used for chain extensions of the polyenes by Wittig or Horner-Emmons type reactions (Sec. 2.1.2). Knovenagel condensation of **114** with malononitrile gave the shortest member of the polarized polyene series (Sec. 2.2), and it is also used for the preparation of terminal acetylenes (Sec. 2.5) and the thio compounds (Sec. 2.4), i.e. it is a truly universal substrate.



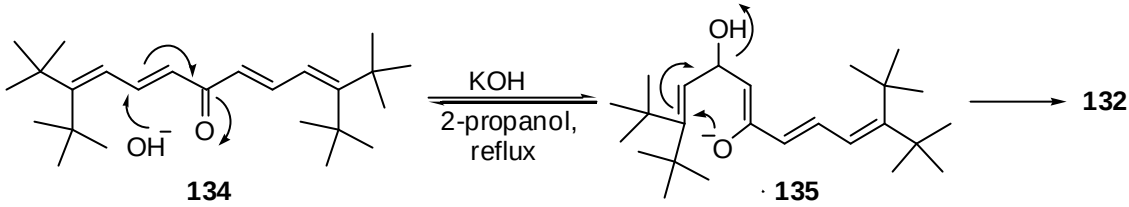
2.1.1.a Synthesis and photochemistry of 2H-pyran (132)

The formation of the side products **131** and **132** during the course of the above reaction can be explained by an aldol type condensation between **114** and acetone which is formed during the reaction. To prove this assumption, the aldehyde **114** was deliberately allowed to react with acetone under basic conditions. A mixture of **114** and acetone was prepared and one half of this mixture was added to a stirred 2.5 M aq. solution of NaOH in EtOH. After 15 minutes of stirring the other half of the mixture was added and the mixture was allowed to stirr overnight at room temperature. The reaction yielded 23% of the methyl

ketone **131** and 69% of the *trans*-ketone **134** (Exp. 4.3.5). No formation of the 2H-pyran derivative **132** was observed.

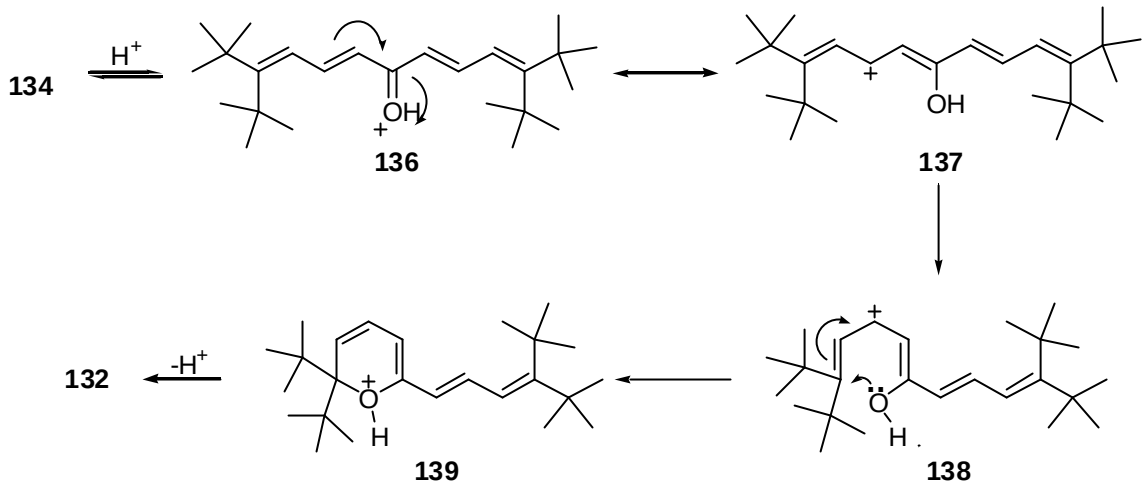


However, when a solution of **134** in 2-propanol was added to an aq. solution of 1M KOH and the mixture refluxed like in the case of the Hass-Bender procedure, conversion to **132** began. This can be explained by a Michael type addition of the hydroxide ion to **134** followed by ring closure of the resulting enolate ion **135** with concomitant loss of hydroxide (Scheme 33). An analogous base-catalyzed isomerization of an allenic ketone to a 2H-pyran derivative has been reported by Krause.[57]



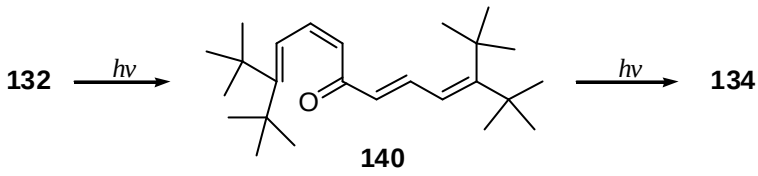
Scheme 33. Base catalyzed cyclization of *trans*-ketone **134** to the 2H-Pyran **132**.

The conversion of the ketone **134** to **132** was also accomplished under acidic conditions. Towards this end a solution of **134** in benzene-d_6 in the presence of a catalytic amount of *p*-toluenesulfonic acid (PTSA) was heated at 60 °C and the conversion of **134** to **132** was conveniently monitored by ^{1}H NMR spectroscopy. The acid catalyzed reaction can be explained by initial protonation of **134** at the carbonyl oxygen followed by cyclization of the intermediate carbenium ion followed by proton loss (Scheme 34).



Scheme 34. Acid catalyzed cyclization of *trans*-ketone **124** to the 2H-Pyran **122.**

Pyran **132** is a greenish yellow solid and very stable in the solid state. Also its chloroform solution is thermally stable for several days at room temperature. However, exposure of the solution to day light for extended periods or deliberate photolysis resulted in the retrocyclization to the *trans*-ketone **134**. This conversion of **132** to the *trans*-ketone **134** presumably takes place through the formation of *Z,E*-dienone **140** intermediate which undergoes a photochemical *cis-trans* isomerization to **134** (Scheme 35). To prove this assumption photolysis of **132** was carried out in $CDCl_3$ and the reaction was followed by ^1H NMR spectroscopy. The disappearance of the signals due to **132** with the concomitant appearance of signals due to **134** were observed. And besides the signals of **132** and **134** signals with very low intensity, which probably belong to **140**, were observed. This assignment was based on signal multiplicity and coupling constants. However, **140** was not formed in sufficient amount for isolation and characterization, probably because of its further isomerization to **134** under photolytic conditions. After prolonged photoylsis the conversion of **132** to **134** was complete and only the signals due to **134** could be observed in the NMR spectrum. The photolysis of the *trans*-ketone did not lead back to the formation of the 2H-pyran derivative.



Scheme 35. Retrocyclization of **122** to **124** by photolysis.

The 2H-pyran derivative **132** is highly fluorescent. Its absorption and fluorescence emmision spectra were measured in two solvents with differring polarities, cyclohexane and acetonitrile. In both solvents the absorption spectrum of compound **132** exhibited π? π^* transitions in the 300-400 nm region (Fig. 1). Several bands with partially resolved vibrational fine structure were observed in both solvents although the resolution of the vibrational fine structures was better in cyclohexane (Fig. 1A) than in acetonitrile (Fig. 1B). The absorption maxima in both these solvents are nearly the same which shows that there is no significant solvatochromism. The solvent polarity thus does not have a significant effect on the ground state of **132**.

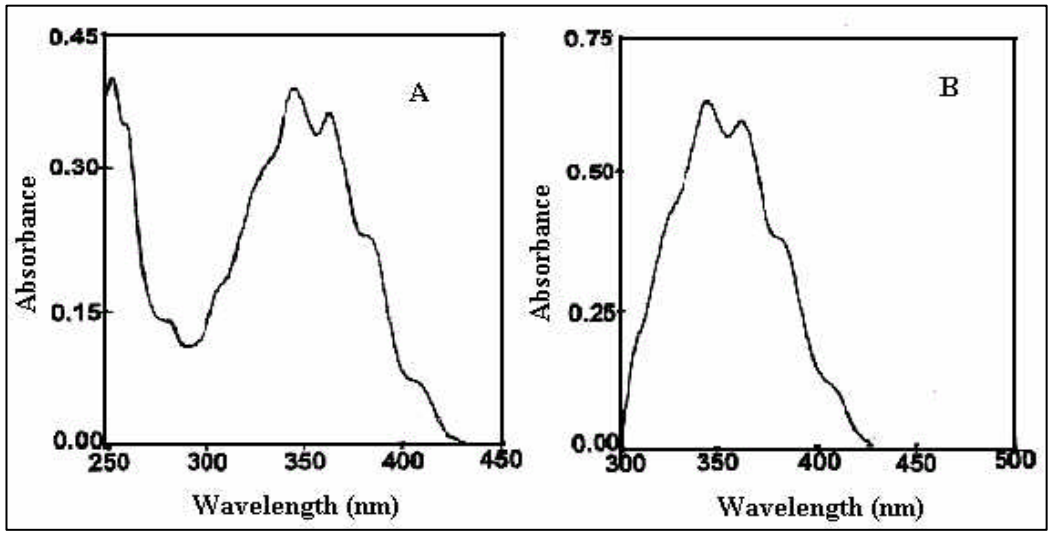


Figure 1. Absorption spectrum of compound **132** in cyclohexane (A) and in acetonitrile (B).

The fluorescence spectra were measured by excitation of the sample at 350 nm, corresponding to the most intense band ($\nu_{0\text{-}3}$). The excitation and emission spectra in cyclohexane and acetonitrile are represented in Fig. 2. There is a significant solvent effect

on the emission spectrum. The fluorescence spectrum shows vibrational fine structure in cyclohexane (Fig. 2A). There is also mirror image relationship of absorption and emission spectra (Fig. 1A and Fig. 2A). The $\nu_{0\text{-}0}$ vibrational bands nearly overlap in the excitation and emission spectra indicating no significant Stoke´s shift. In acetonitrile the resolution of the vibrational bands is poor in both excitation and emission spectra (Fig. 2B) compared to the absorption spectrum in the same solvent. The band width of the excitation and the emission spectra in acetonitrile are smaller then that in cyclohexane. In acetonitrile the emission and excitation spectra have a mirror image relationship.

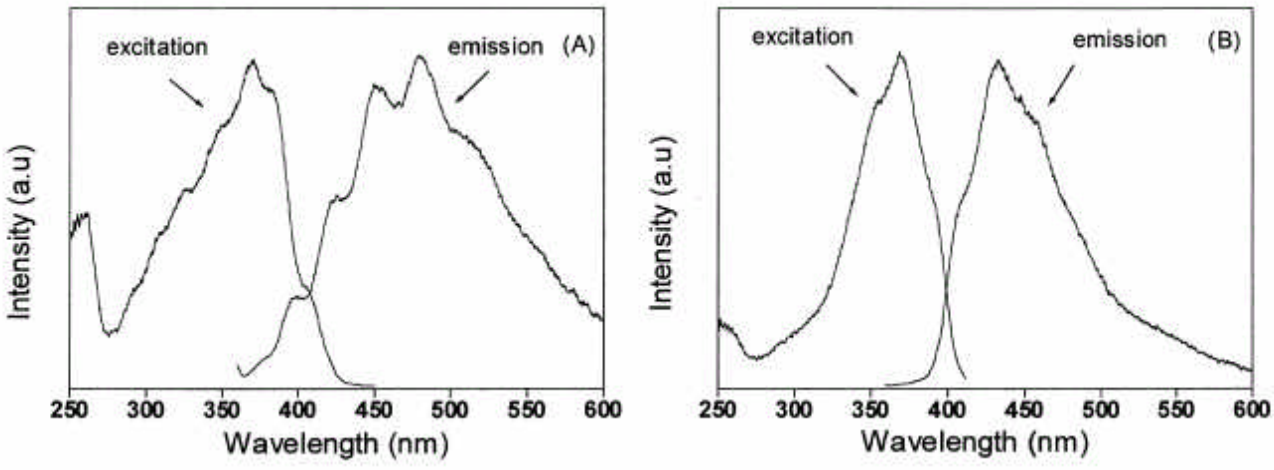


Figure 2. Fluorescence emission and excitation spectra of **132** in cyclohexane (A) and in acetonitrile (B).

2.1.2 Synthesis of the polyenealdehydes up to 10 double bonds

The chain extention of the polyenealdehydes of type **47** have been studied by Hopf and co-workers for several years. First C. Mlynek has extended the series up to two which was followed by D. Klein up to six double bonds, and both used Wittig reactions for chain extensions. In the present work the polyene chain was extended up to 10 double bonds and not only by Wittig reactions but also by the Horner-Emmons variation of the Wittig type reactions. By the Wittig reaction one double bond was added to the polyene systems in each step whereas by a Horner-Emmons variation the aldehydes were extended by the addition of two or three double bonds at once.

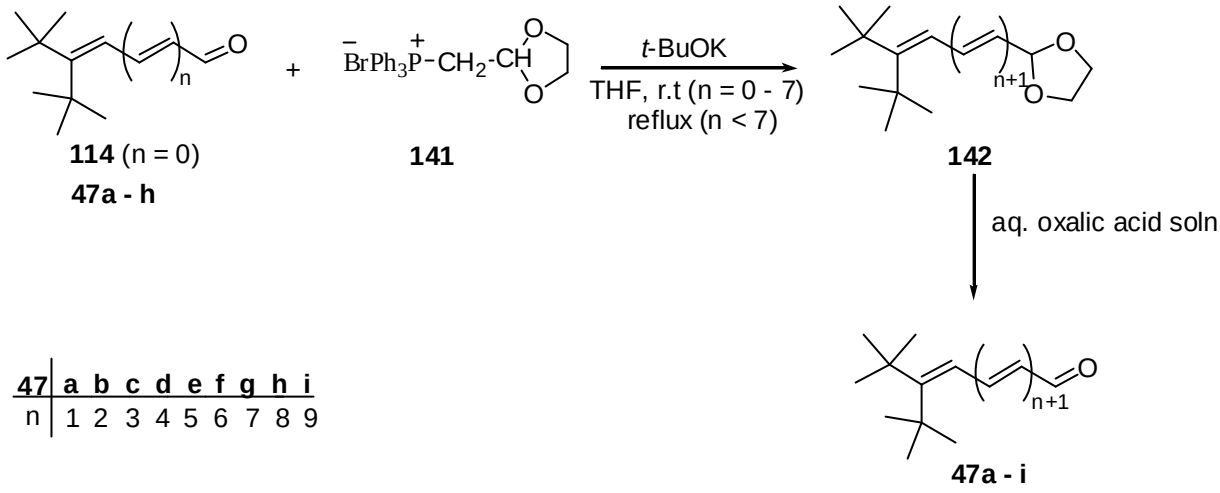
2.1.2.a Chain extensions by Wittig reactions

The Wittig reaction is one of the most useful synthetic methods to prepare alkenes. It was first reported by Wittig and Geissler in 1953 when they discovered that the reaction between triphenylmetheylenephosphorane and benzophenone gave 1,1-diphenylethene and triphenylphosphine oxide in almost quantitative yield.[12] As mentioned earlier this unusual reaction between carbonly compounds and triphenylalkylydines which provides the alkenes in excellent yields quickly found great interest for the synthesis of polyenes. From the stereochemical point of view it is often stated that the Wittig reaction does not always give a single isomer, but there are also quite a few reports which describe the formation of only one isomer. In this work the Wittig reaction carried out for the chain extensions of polyene aldehydes only led a single isomer, namely the *E* isomer.

The Wittig reactions for the chain extensions were performed by reacting one equivalent of the necessary aldehyde (**114**, **47a-i**) with the phosphorus ylid prepared in situ by the treatment of 2.5 equivalents of the Wittig salt [(1,3-dioxalane-2-yl)methyl]-triphenylphosphoniumbromide **141**[*] with 2.4 equivalents of *t*-BuOK in THF (Exp. 4.3.7-15). All Wittig reactions other than the reactions of the aldehydes **47g - h** (8 and 9 double bonds) were carried out at room temperature. After several hours of stirring the reaction mixtures were treated with aq. oxalic acid solution to remove the acetal protection and stirring continued overnight. After aqueous work up purification of the compounds were carried out by column chromatography on silica gel. The product yields up to the aldehyde **47h** were all quantitative. The aldehydes **47a - f** are highly soluble and also stable as long as they are kept under N_2 gas and in the cold. Starting with aldehyde **47g** (8 double bonds) the solubility of the aldehydes decreased dramatically, and it was not possible to carry out the reactions at room temperature anymore. Rather for the last two reactions, the preparation of aldehydes **47h** and **47i**, reflux conditions were necessary and

[*] The Wittig salt **131** is commercially available but can also be quite easily prepared by reacting 1 equivalent of 2-(bromomethyl)-1,3-dioxalane with 1 equilvalent of triphenylphosphine for 84 hours at 70 °C.

still during the reflux process it was possible to observe undissolved crystals. The reflux conditions and the insolubility of the aldehydes resulted in low product yields (~ 55%). Also, after chromatographic purification of the products **47h** and **47i** no unreacted starting material was recovered, showing that decomposition or polymerization took place.



114 (n = 0)
47a - h

141

142

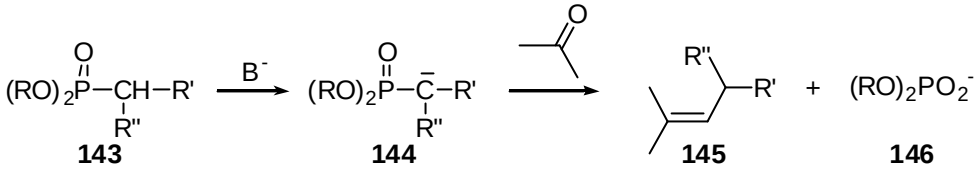
47	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**
n	1	2	3	4	5	6	7	8	9

47a - i

Like for all polyene systems the effect of the chain length increase was very obvious from the absorption spectra of the aldehydes. While the smallest member of the series displayed an absorption maxima at 246 nm and the first two memebers (**114**, **47a**) were colourless, starting with three double bonds (**47b)** the colours of the aldehydes began to change from yellow to very dark red and the absorption maxima increased up to 464 nm. The UV/Vis absorption spectra of the aldehydes are discussed separately in Sec. 2.3.

2.1.2.b Chain extensions by Horner-Emmons reactions

Wittig type reactions that are carried out by the ylids prepared from phosphonates **143** instead of phosphines are generally referred to as *Horner-Emmons*, *Wadsworth-Emmons* or *Wittig-Horner* reactions.[58] That the ylids of the phosphonates **144** are much more reactive than the phosphoranes is an advantage of these reactions. And in addition because the phosphorus containing product formed is a phosphate ester **146**, which is soluble in water, it is much easier to separate it from the olefin product by aqueous work-up (Scheme 36).

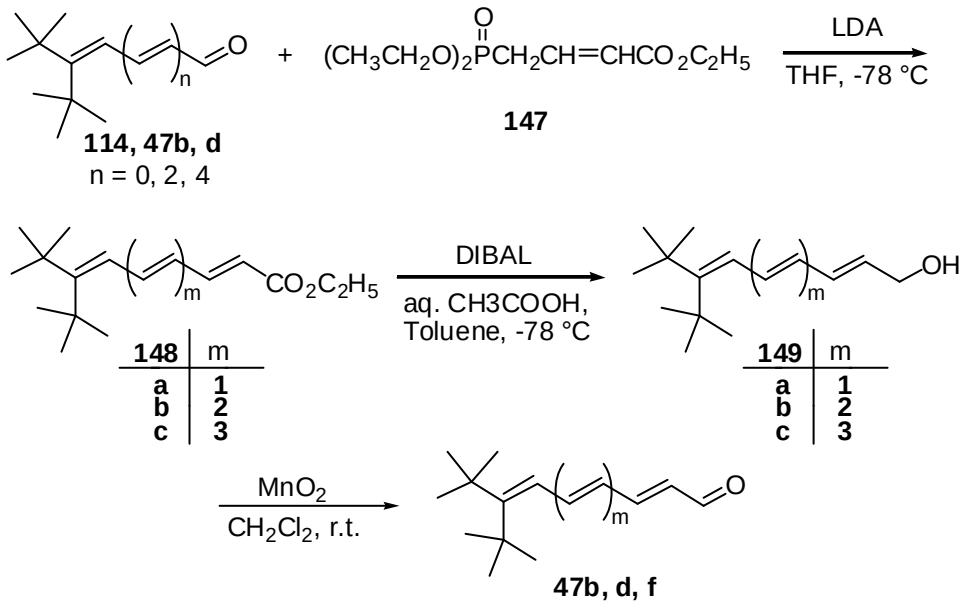


Scheme 36. Horner-Emmons type reactions.

In the long chain polyene synthesis using the Horner-Emmons type reactions it was possible to extend the aldehydes by two or three double bonds in one step[58, 59] employing either an already available or an easily synthesised phosphonates (by Arbuzov reactions). To show that one can extend the polyene aldehydes with the desired stereochemistry (*E* isomer in this case) in good yields and in less time in comparison with the Wittig reactions, the aldehydes **114, 47b** and **47d** (1, 3, 5 double bonds) were reacted with the commercially available phosphonocrotonate **147**. Treatment of the phosphonate with LDA at −78 °C in THF followed by the addition of the aldehyde to the reaction mixture gave the desired ester **148**. The reactions were completed in about 1.5 h when the temperature had reached to 0 °C, and during aqueous work up the phosphate ester was easily removed. The purification of the products was carried out by column chromatography on silica gel. In all three cases the polyene esters were formed in quantitative yields and exclusively as all-*E* isomers as shown by the ^{1}H NMR coupling constants (Exp. 4.3.16, 19, 22). While the polyene ester **148a** is a colourless oil at room temperature, the ester **148b** is a yellow low melting solid and **148c** is a orange coloured solid. All the three esters are highly stable when kept below 0 °C.

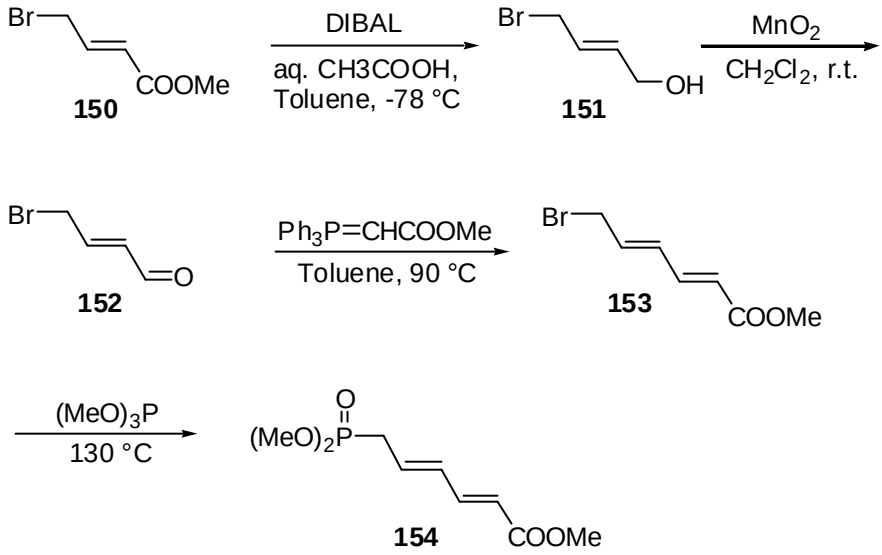
The second step consisted in the reduction of the esters with DIBAL at −78 °C in toluene to the polyene alcohols **149** (Exp. 4.3.17, 20, 23). The polyenealcohols are the least stable compounds of the polar polyenes studied in this work. Reduction reactions were carried out by using 1 to 3 equivalents of the esters and DIBAL, respectively. When adding the first drops of DIBAL the colour of the reaction mixtures darkend. By the further colour change it was easy to observe the end of the reaction because when all starting material had been reduced the very dark coloured solutions bleached back to very light colours, colourless for the reduction of **148a**, yellow for **148b** and light orange for **148c**. When the colour change was complete the unreacted DIBAL was destroyed with aqueous 50% acetic acid solution at −78 °C, cooling was removed, and the mixtures were directly

filtered through celite and washed several times with acetone. After removal of the solvent and trying out purification by column chromatography or letting the products stay in the freezer for short times immediate polymerization was observed, thus it was necessary to use the alcohols for further reactions quickly. MnO_2 oxidation of vinylic alcohols is a well know method for the preparation of unsaturated aldehydes[60] and in this case also it was the preferred method. The alcohols **149a - c** were reacted with 40 equivalents of MnO_2 in CH_2Cl_2 at room temperature for 3 hours. After filtration through celite and chromatographic purification on silica gel the aldehydes **47** were obtained (Exp. 4.3.18, 21, 24). It is necessary to mention that the instability of the alcohols **149** plays a very important role in this synthetic route, and although the first Horner-Emmons and the last MnO_2 oxidation reactions gave very high yields, the overall yield of the aldehydes remained around 50% only, whereas in two different Wittig reactions, as explained in the previous section (Sec. 2.1.2.a), it was possible to obtain the same aldehyes with yields higher than 80%.



With the same strategy but by using a phosphonate ester with one additional double bond unit, namely (2*E*,4*E*)-6-(dimethoxyphosphinyl)-2,4-hexadienoate (**153**), it was possible to add three double bonds in one step to the polyene systems. However because (2*E*,4*E*)-6-(dimethoxyphosphinyl)-2,4-hexadienoate is not commercially available it is necessary to

prepare it starting from methyl 4-bromocrotonate **150.** In the first step the ester was reduced with DIBAL at −78 °C, followed by MnO_2 oxidation to 4-bromo-crotonaldehyde **152**. Wittig reaction of **152** with (methoxycarbonylmethylene)triphenyl-phosphorane then gave 6-bromo-2,4-hexadienoicacid methylester (**153**), and the last step was an Arbuzov reaction of **153** with trimethyl phosphite to yield **154**.[59] Although the phosphonate ester **154** could be prepared with an overall yield of 70% on the mg scale, this sequence is not adaptable to larger scales, which is a big disadvantage of this approach.

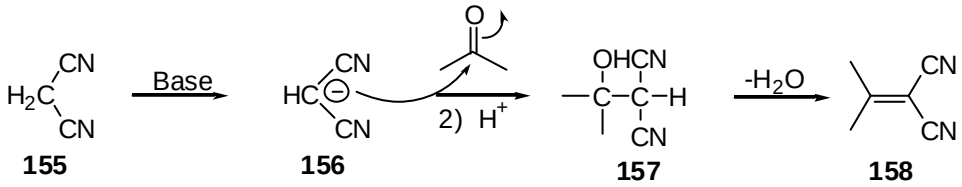


The Horner-Emmons reaction between the aldehyde **47b** and **154** gave the same result as in the case of the preparation of the ester with 5 double bonds when phosphonocrotonate was used. However, because of the small available amount of the phosphonate, this reaction was not applied further. Overall, the lower yields that were obtained from the Horner-Emmons reactions in comparison to the Wittig reactions are definitely a disadvantage for their application in the preparation of a series of long chain polyenes.

2.2 Dicyano functionalized polyenes

As mentioned earlier conjugated π-electron systems are well known to show exceptionally large nonlinear optical susceptibilities and it has been reported that extension of the conjugation length and the introduction of electron withdrawing cyano groups at the terminal position(s) results in an improvement of the NLO porperties. The increased bathochromic shift caused by the introduction of cyano group also opens the possibility to use such systems as dye stuffs.[43-46]

The most convenient method to introduce cyano groups at the terminal positions of a polyene system is the Knoevenagel type condensation of the polyene aldehydes with malononitrile (**155**). The Knoevenagel condensation is a type of aldol reaction catalyzed by weak organic bases, usually pyridine, piperidine, or amino acids.[61] The reaction is defined as the reaction of a ketone or aldehyde with a methylene group of enhanced acidity, as it is the case with malononitrile. The two step process starts with the attack of the carbanion on the carbonyl group of the aldehyde/ketone forming a *b*-hydroxy intermediate **157** followed by a dehydration step (1,2-elimination) to yield the *a*,*b*-unsaturated product **158** (Scheme 37). The reaction is solvent dependent and polar solvents (alcohol or aqueous alcohol) are reported to facilitate the first step and suppress the elimination step.



155 **156** **157** **158**

Scheme 37. Mechanism of the Knoevenagel condensation reaction.

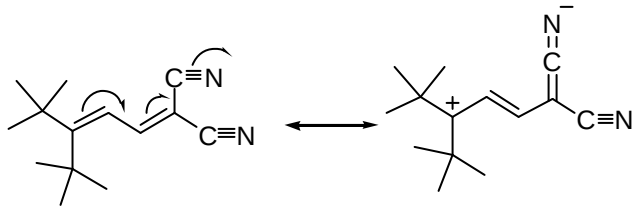
The aldehydes **114** and **47a - i** were all reacted with malononitrile under Knoevenagel conditions and a series of dicyano terminated polyenes up to 11 double bonds (**159** to **168**) were prepared (Exp. 4.3.25 - 34). The reactions were performed by using equimolar of aldehyde and malononitrile and 1/100 molar equivalents of *b*-alanine as the catalyst. Reactions of the aldehydes with 1 to 7 double bonds (**114**, **47a - f**) in refluxing 95% ethanol gave the desired products in more than 90% yield. However, because of solubility

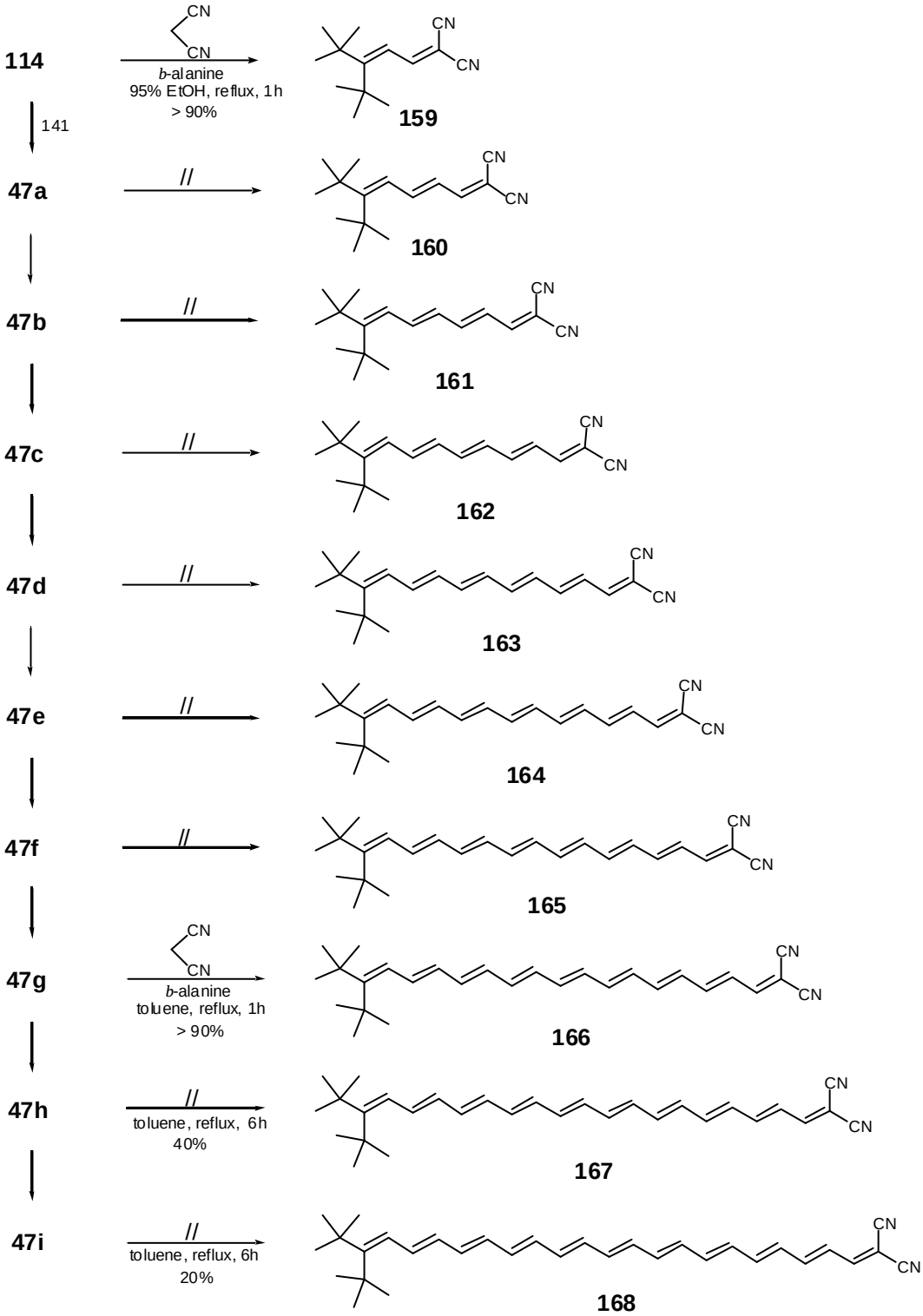
problems of the aldehydes with 8, 9 and 10 double bonds (**47g - i)** as mentioned previously (Sec. 2.1.2.a), it was necessary to change the solvent from ethanol to toluene for the reactions with these aldehydes. While the reaction of **47g** with malononitrile in refluxing toluene gave the product **166** again in quantitative yield, in the reaction with **47h** the yield decreased to 40% and with **47h** it was only 20% despite the change of solvent and increased reaction times from 1 to 6 hours. In this last two reactions after chromatographic purifaction on silica gel no starting material was recovered despite the very low yields of product formation. Other than the last two members of the series, **167**, **168** which were purified by chromatography, all other vinylogs were purified by recrystallization from hexane.

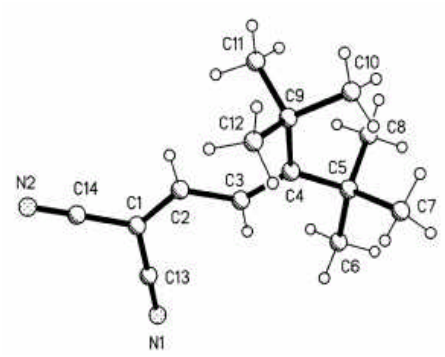
The solubility problems faced with the aldehydes were not noted with the dicyano derivatives, and all are highly soluble in polar solvents. They are also highly stable towards heat and air. They can be kept for months or years at room temperature. The solutions of the compounds are also very stable even under daylight. The bleaching of the dichloromethane solutions of the compounds were observed to start only after a year. Their UV/Vis absorption spectra are discussed on the following pages (Sec. 2.3).

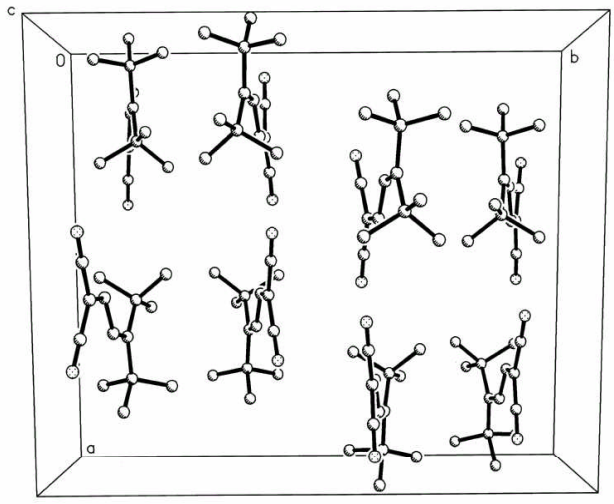
The dicyano functionalized polyenes gave nice crystals upon recrystallization from hexane and the X-ray analyses of the first three members of the series **159**, **160**, and **161** were carried out. The single crystal structures and their packing diagrams are shown in figures 5, 6 and 7.

In Table 1 a comparison of the bond lengths of the polarized polyenes **159**, **160**, **161** with those of the unpolarized polyenes **48a**, **48b**, **50** is given. The bond length of the C-C double bonds bearing the tert-butyl substituents in the polarized polyenes are consistantly longer by 0.5 pm compared to the C=C bond length in the non-polarized polyenes. Furthermore the C-C single bond lengths are consistantly 1.5 pm shorter then the corresponding bonds in the non-polarized polyenes. These observed consistancy in the bond lengths can be attributed to the contribution of the resonance structure in the polarized polyenes as shown below.



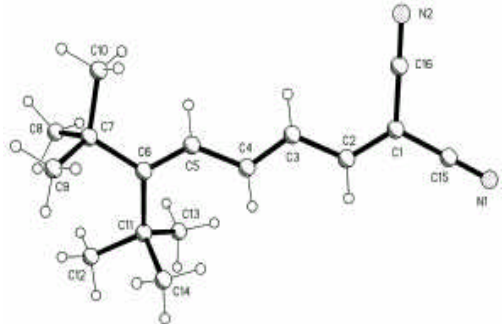

114
CN
CN
b-alanine
95% EtOH, reflux, 1h
> 90%
159
141
47a
//
160
47b
//
161
47c
//
162
47d
//
163
47e
//
164
47f
//
165
47g
CN
CN
b-alanine
toluene, reflux, 1h
> 90%
166
47h
//
toluene, reflux, 6h
40%
167
47i
//
toluene, reflux, 6h
20%
168

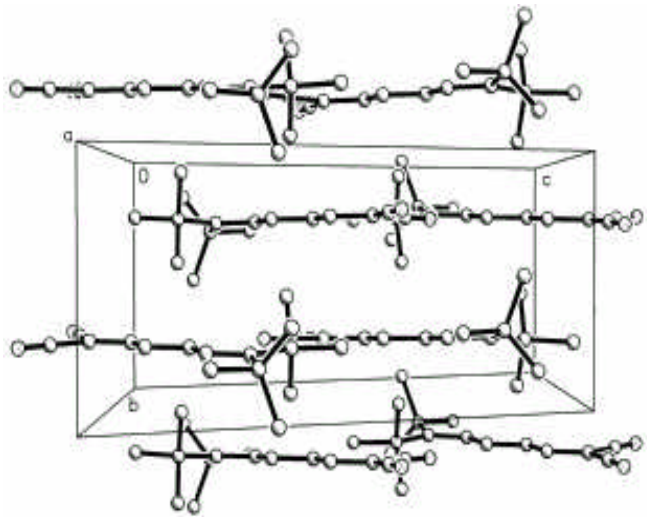




Unit cell dimensions: a = 1510.2 (2) pm, b = 1850.1 (3) pm, c = 986.1 (2) pm; $\alpha = 90°$, $\beta = 98.40\ (2)°$, $\gamma = 90°$.

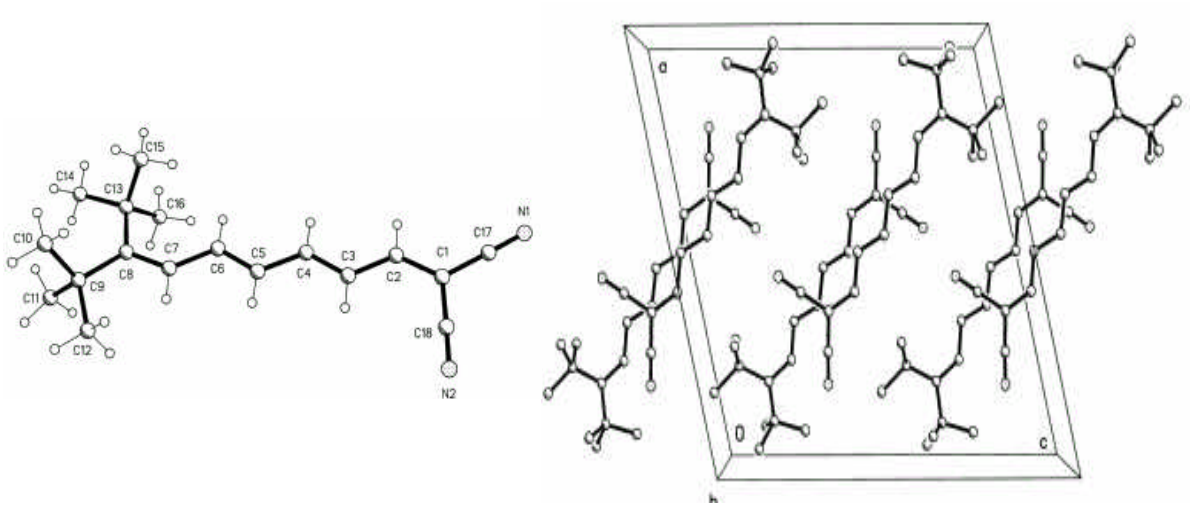
Figure 3. Structure of **159** in the crystal and its packing diagram.





Unit cell dimensions: a = 1532.5 (3) pm, b = 677.2 (2) pm, c = 1572.1 (3) pm; $\alpha = 90°$, $\beta = 114.336\ (10)°$, $\gamma = 90°$.

Figure 4. Structure of **160** in the crystal and its packing diagram.



Unit cell dimensions: a = 1605.9 (3) pm, b = 672.4 (8) pm, c = 1612.8 (2) pm; α = 90°, β = 104.79 (3)°, γ = 90°.

Figure 5. Structure of **161** in the crystal and its packing diagram.

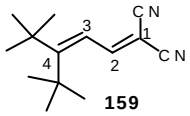
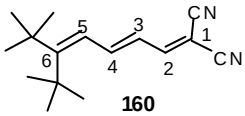
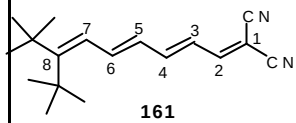
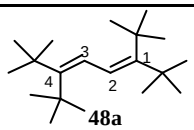
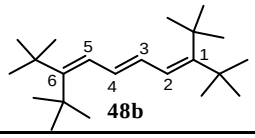
	C1-C2	C2-C3	C3-C4	C4-C5	C5-C6	C6-C7	C7-C8
 **159**	134.7 (4)	143.3 (4)	135.5 (4)				
 **160**	135.3 (3)	142.2 (3)	135.4 (3)	143.8 (3)	135.5 (3)		
 **161**	136.6 (2)	140.6 (2)	136.0 (2)	141.2 (2)	135.7 (2)	143.6 (2)	135.6 (2)
 **48a**	134.9	145.8	134.9				
 **48b**	135.0 (2)	145.4 (2)	134.4 (2)	145.4 (2)	135.0 (2)		
 **50**	134.9 (2)	145.0 (2)	133.6 (2)	144.0 (3)	133.6 (2)	145.0 (2)	134.9 (2)

Table 1. Bond lengths of tert-butyl substituted polyenes.[23b]

2.3. UV/Vis absorption properties of polyenes

The absorbtion of ultraviolet and/or visible radiation results in the excitation of electrons from the ground state to higher energy levels. The electrons of an organic molecule that contribute to absorption are (1) those which participate directly in bond formation between atoms, and (2) nonbonding or unshared outer electrons that are largely localized at atoms such as oxygen, nitrogen, sulfur, and the halogens. Most applications of absorption spectroscopy to organic compounds are based on transitions of the *n* or π electrons to the π^* excited state ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions). This is because the energies required for these processes bring the absorption peaks into an experimentally convenient accessible spectral region, 200 to 700 nm. Obviously the requirement for both of these transitions is the presence of an unsaturated functional group which will provide the π orbitals. The term *chromophore* is given to these unsaturated absorbing centers.[62]

The molar absorptivities for peaks associated with $n \rightarrow \pi^*$ transitions are generally low and ordinarily range from 10 to 100 L mol^{-1} cm^{-1}. The values for $\pi \rightarrow \pi^*$ transitions however normally fall in the range between 1000 and 10000. Another characteristic difference between the two types of absorption is the solvent effect on the absorption maximum. Bands associated with $n \rightarrow \pi^*$ transitions are generally shifted to shorter wavelengths (blue shift) with increasing polarity of the solvent. Usually, but not always, the reverse trend (red shift) is observed for $\pi \rightarrow \pi^*$ transitions. The blue shift arises from the increased solvation of the unbonded electron pair, which lowers the energy of the n orbital. The most dramatic effects (30 nm or more) are seen in polar hydrolytic solvents such as water or alcohols, where hydrogen bond formation between the solvent protons and the nonbonded electron pair is extensive. With the red shift, attractive polarization forces between the solvent and the absorber tend to lower both the unexcited and excited state energy levels. However, the effect on the excited state is greater and the energy differences thus become smaller with increased solvent polarity causing small red shifts.[63, 64]

In the molecular orbital treatment, π electrons are considered to be further delocalized by conjugation. The effect of this delocalization is to lower the energy of the π^* orbital and give it a less antibonding character. As a consequence absorption maxima are shifted to

longer wavelengths. The wavelengths of absorption peaks for conjugated systems are sensitive to the types of groups attached to the doubly bonded atoms. The presence of cyano groups, doubly bonded oxygen of aldehydes, ketones, and carboxylic acids in conjugation with an olefinic double bond are known to shift the absorption maxima to longer wavelengths. Various empirical rules have been developed for predicting the effect of substitutions on absorption maxima and have proved useful for structural determinations.[65]

Absorption spectra of polyenes in the region from ultraviolet to visible in the condensed phase (liquid, solid, solutions etc.) are very broad in most cases. Thus, bands arising from distinct vibronic transitions are not resolved. However, the spectra of polyenes in hydrocarbon environments at low temperature or in supersonic expansions show vibrational fine structures. The UV/Vis absorption spectrum of a polyene shows an intense absorption band and an extremely weak absorption band which is hidden below the strong absorption band. This spectral pattern is a general property of linear polyenes of all chain lengths independent of local symmetry and/or the presence of *cis* bonds.[66]

2.3.1. Polyene aldehydes

The UV/Vis absorption properties of polyenealdehydes containing up to 6 double bonds (**114**, **47a - e**) have been investigated and reported in the literature.[23b] The absorption bands are very broad showing no vibrational fine structures. Bands from the $n \rightarrow \pi^*$ transitions are hidden under the very broad bands formed from the $\pi \rightarrow \pi^*$ transitions. As expected, with an increase of the chain length the absorbance shifts to longer wavelengths. However, after 6 double bonds the red shift trend shows a decrease. This is a well known phenomenon for polyenes and has been also shown by theoretical calculations. In the case of polyenes with a large number of conjugated double bonds the C-C double bonds are less double bond in character and the single bonds are correspondingly more double bond in character. This causes the two kinds of bonds to become more and more alike and as a result after some point the increase in the chain length starts to cause less bathochromic shift.[67] As can be seen from Figure 6 the increasing trend of absorption at longer wavelengths starts to show a decrease around 7

double bonds and the difference between the absorbance maxima of the compounds with 9 and 10 double bonds gets very small indeed.

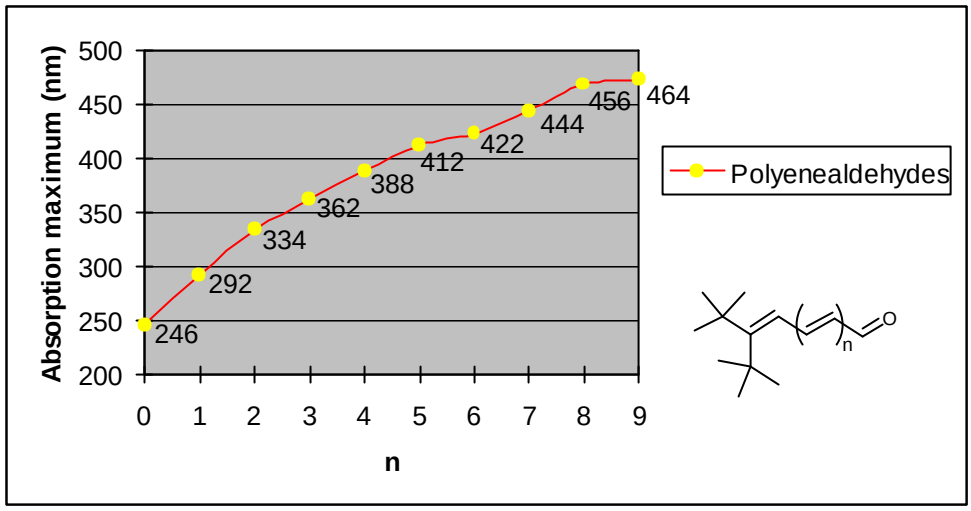


Figure 6. Increase in the absorption wavelength of polyene aldehydes as a function of chain length.

The effect of increased chain length is visible by the colours of the aldehydes, which changed from light yellow (n = 2) to very dark wine red (n = 9).

2.3.2. Dicyano functionalized polyenes

The absorption spectra of the dicyano polyenes are similar to those of the polyene aldehydes. The compounds absorbed at higher wavelengths with increasing chain length. The effect of the cyano groups were as excpected and resulted in much more intense absorption bands in the visible region. The bands of $n \rightarrow \pi^*$ transitions were hidden by the broad absorption bands of the $\pi \rightarrow \pi^*$ transitions. Starting with the compound with 7 double bonds the red shifts began to decrease, and the compounds with 10 and 11 double bonds absorbed at approximately the same wavelength, at 556 nm (Fig. 7).

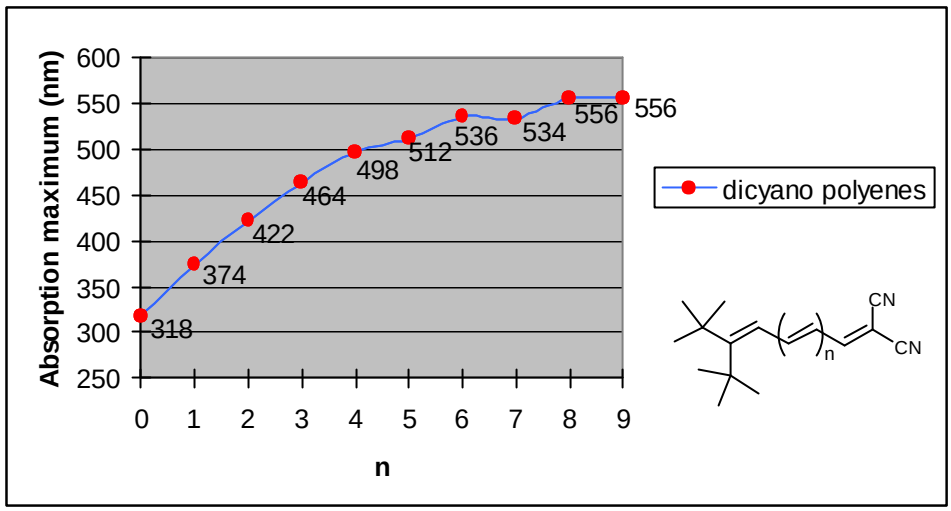


Figure 7. Increase in the absorption wavelength of dicyano polyenes as a function of chain length.

The HOMO - LUMO energy differences calculated by AM1 Semi-empirical calculations, PC SPARTAN Pro Version 1.0.1, showed a very similar trend as the experimental transition values. The calculated HOMO - LUMO energy gaps became smaller with increasing number of double bonds and starting with 7 double bonds the decrease of the values leveled off (Fig. 8). The theoretical calculations refer to the gas phase, whereas the experimental values were determined in solution.

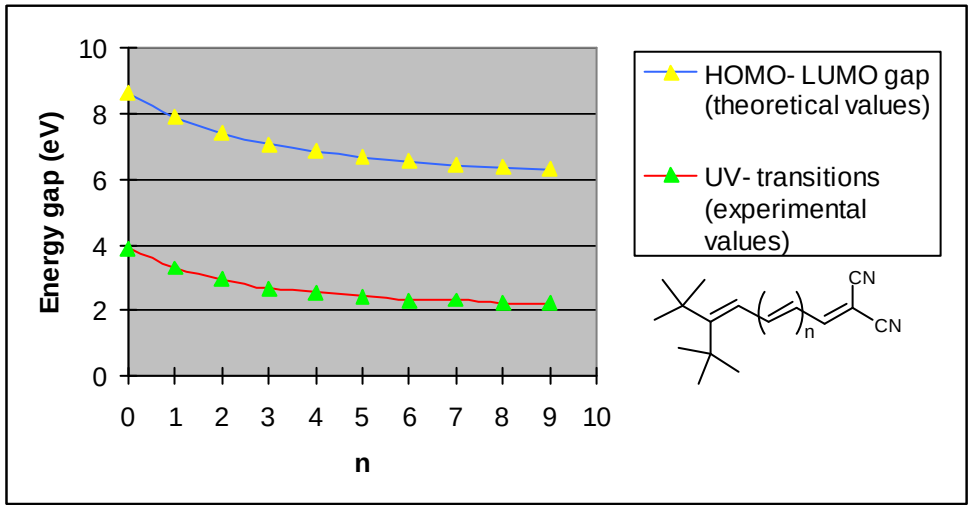


Figure 8. Theoretical and experimental HOMO- LUMO energy difference as a function of chain length.

The increase in chain length effected the colour of the compounds **159** to **167** (2 to 10 double bonds) very significantly. Picture 1 shows the dichloromethane solutions of these compounds. However, in the solid state the colour change could not be observed very well, because starting from compound **163** (6 double bonds) all crystals appeared black. In the solid state the shortest member of the series (2 double bonds) was colourless and the colours were yellow, orange and dark red for 3, 4, and 5 double bonds, respectively.

Picture 1. Solutions of the dicyano polyenes in dichloromethane. Colour change as the chain length is increased from 2 to 10 double bonds.

To determine solvent effect on these systems, compounds **162** and **164** (5 and 7 double bonds) were studied in 5 different solvents with differing polarities. No significant solvatochromism was detected. The maximum observed red shift was 20 nm for the compound with 5 double bonds. For the compound with 7 double bonds it was 26 nm (Table 2). In polar solvents no vibrational fine structure was detected, the bands were very broad. However, the small solvent effect of the non-polar solvents on the polar compounds resulted in partly resolved spectra. The vibrational levels were less affected due to solvation when CCl_4 or hexane were used (Fig. 9 and 10).

	Hexane	CCl_4	CH_2Cl_2	CH_3CN	EtOH
5 double bonds	446	445	458	444	446
7 double bonds	480	494	506	486	486

Table 2. Maximum absorption wavelengths (in nm), in solvents with different polarities.

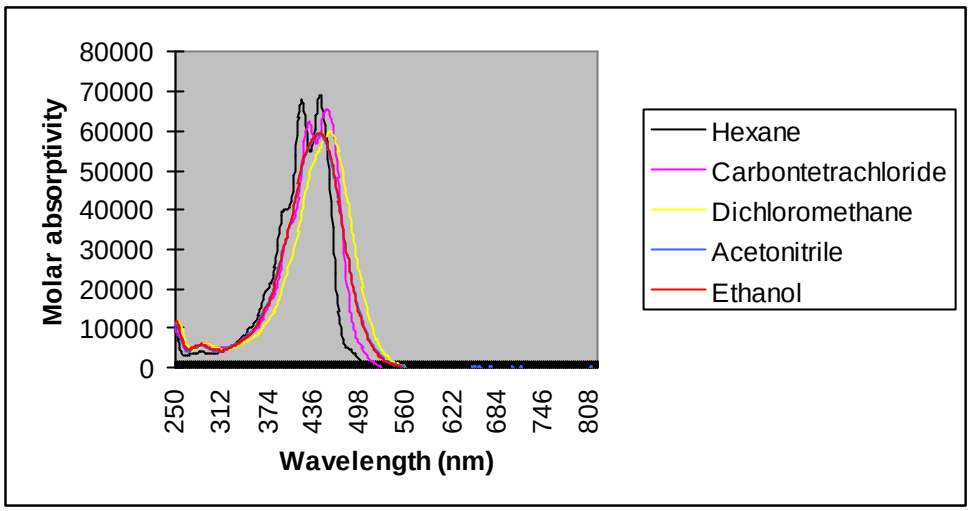


Figure 9. Solvent effects on the UV/Vis spectrum of pentaene **162**.

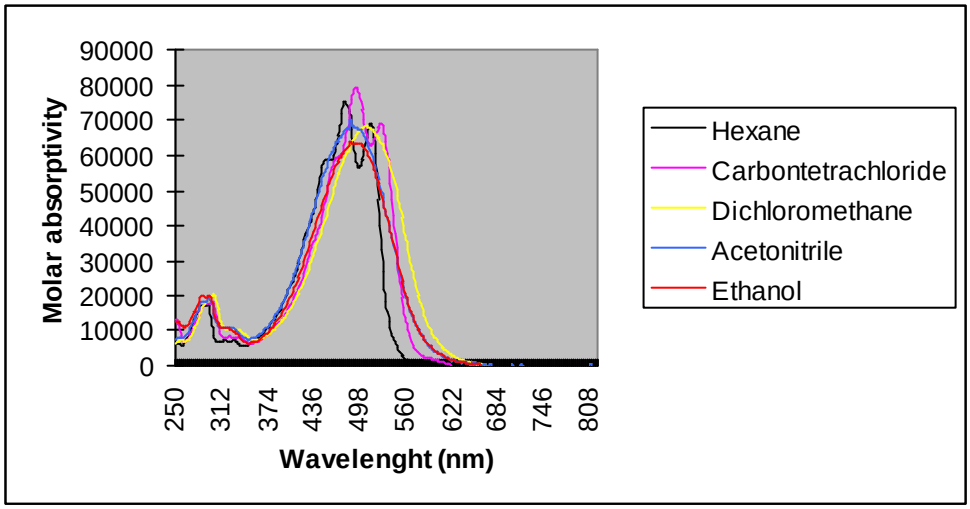


Figure 10. Solvent effects on the UV/Vis spectrum of heptaene **164**.

The effect of the cyano groups on the absorption spectra of polyenes were very significinat. For example whereas the dicyano polyene with 5 double bonds was already dark red in colour and absorbed at 464 nm, the polyenealdehyde absorbed at 464 nm when it had 10 conjugated double bonds in the chain. Another similar system which was studied by Hopf and co-workers was the tetra-*tert*-butyl polyenes and in that series the absorption at 462 nm occured when the compound had 11 conjugated double bonds.

Table 3 shows the absorbance maxima of these three systems which were protected by *tert*-butyl groups.

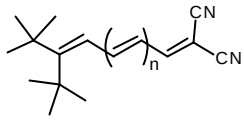
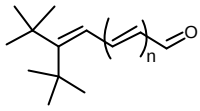
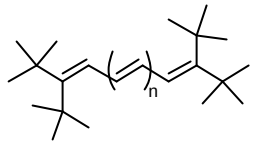
n	[1] 		[2] 
0	318	246[2]	248
1	374	292[2]	294
2	422	334[2]	324
3	464	362[2]	352
4	498	388[2]	376
5	512	412[1]	420
6	536	422[1]	442
7	534	444[1]	432
8	556	456[1]	-
9	556	464[1]	462

Table 3. Absorption maxima (nm) for *tert*-butyl protected polyenes

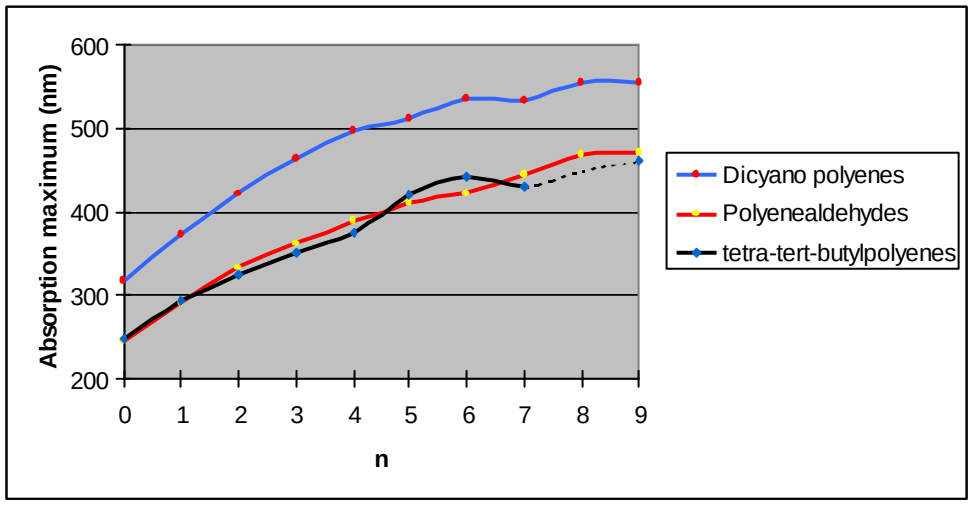
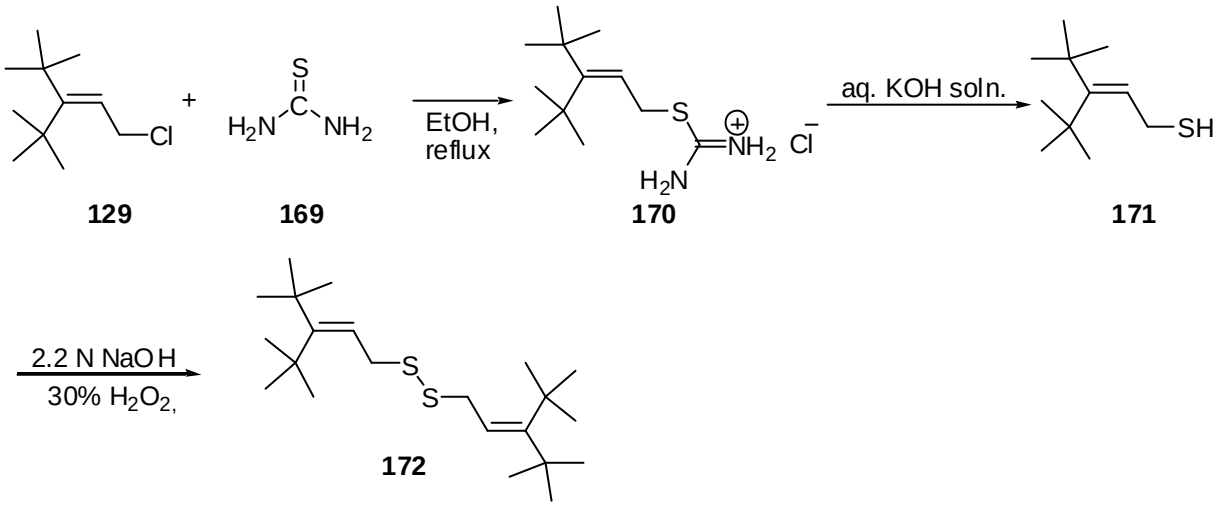


Figure 11. Increase in absorption maxima for the *tert*-butyl substituted polyene systems as a function of end groups.

[1] Chloroform
[2] Acetonitrile

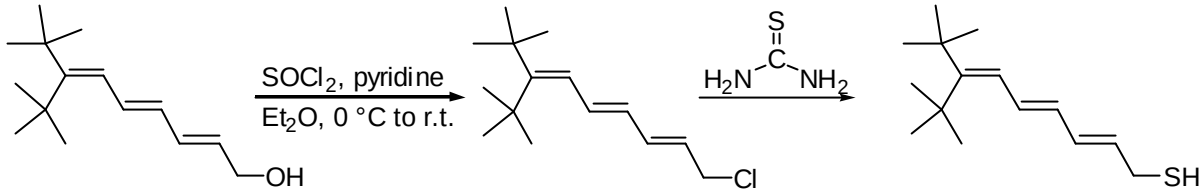
2.4. Thio group functionalized polyenes

The studies described in the previous sections (Sec. 2.1 and 2.2) convincingly demonstrate the stabilizing effect of the bulky *tert*-butyl groups in long chain polyene systems. It was expected that *tert*-butyl groups at one terminus should also stabilize polyenes with a thiol group at the other end. To investigate whether conventional thiol preparation methods are adaptable to our systems, the first reaction was performed with the chloride **129**. Refluxing a mixture of equimolar amounts of **129** and thiourea **169** in ethanol for 3 hours resulted in the formation of white isothiuronium salt **170** which was then cleaved by alkali yielding the thiol **171** quantitatively (Exp. 4.3.35). The thiol **171** is quite stable to air and can be kept for several days without conversion to the disulfide **172**. The disulfide was prepared separately in 100% yield by treating **171** with aqueous sodium hydroxide solution and 30% H_2O_2 (Exp. 4.3.36).[68]



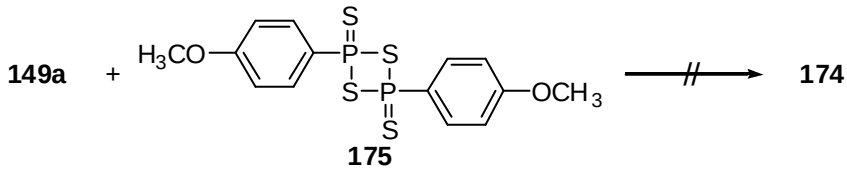
The convenient preparation and the stability of the thiol **171** were unfortunately not encountered for the polyenes with longer chains. In the next reaction the alcohol **149a** was converted to the vinylic halide **173** with thionyl chloride and pyridine in diethylether (Exp. 4.3.37). Already at this stage stability problems started to arise. It was impossible to purify the chloride **173**. After chromatographic separations (TLC or column chromatography on silica gel) only polymer formation was observed. Therefore, **173** had to be reacted further with thiourea without purification. The reaction of **173** with **169**

gave the thiol **174** (Exp. 4.3.38), however, its presence could only be observed by ^{1}H NMR spectroscopy of the crude reaction mixture. While the CH_2 protons of **173** gave a doublet at δ = 3.97 (J = 7.41 Hz), this doublet disappeared in the ^{1}H NMR spectra of the crude product, and a triplet at δ = 3.25, corresponding to the CH_2 protons of **174** and a peak just after the *tert*-butyl peaks at δ = 1.48 that probably belongs to SH proton appeared. The compound decomposed/or polymerized very quickly even under inert gas protection and it was not possible to handle, purify, and characterize it completely.



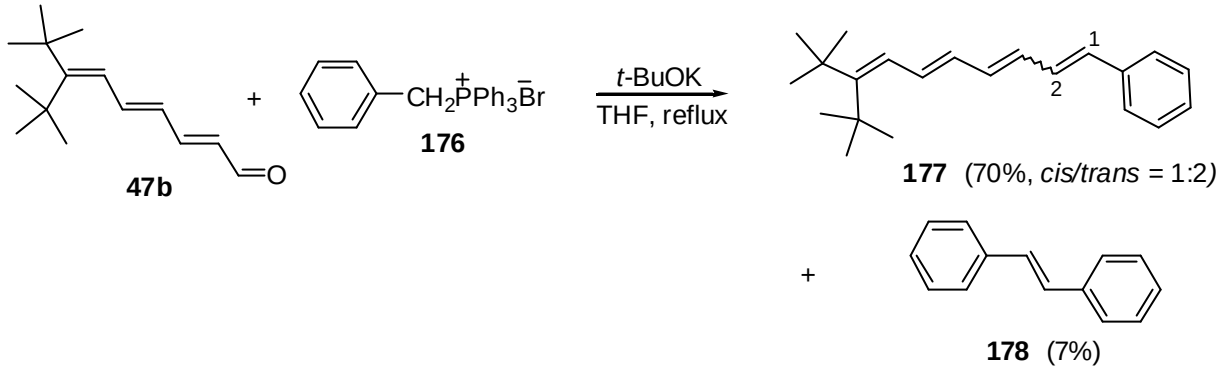
149a **173** **174**

Direct conversion of alcohols to thiols by the use of Lawesson´s reagent **175** has been reported in the literature.[69] However, in this case reacting **149a** with **175** in refluxing toluene provided a mixture of several products which was impossible to purify and, besides, in the ^{1}H NMR spectrum of the crude mixture no signals that could be assigned to the thiol **174** were observed .

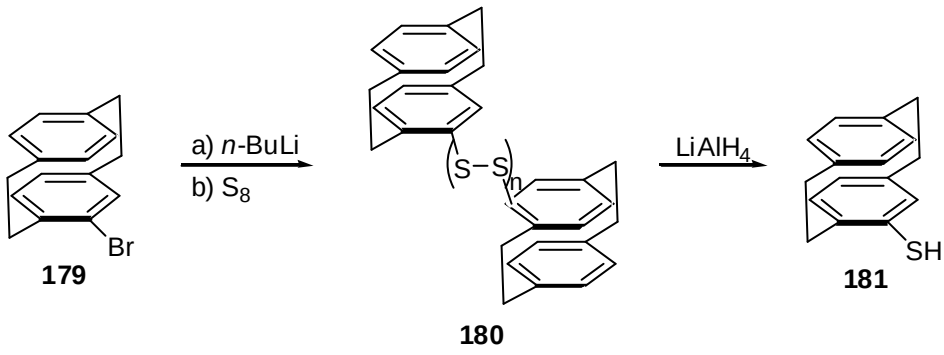


As mentioned earlier, the presence of phenyl rings at the termini of polyene systems are also known to have a stabilizing effect (Sec. 1.1). It should hence be possible to prepare a stable thio-group funtionalized polyene by terminating the polyene system with a phenyl ring having a thiol group at the *para*-postion. To see how stable the systems would be with a phenyl substituent, compound **177** was prepared by a Wittig reaction of the adehyde **47b** with the commercially available Wittig salt **176** (Exp. 4.3.39). The reaction was carried out in refluxing THF and *t*-BuOK was used as the base for ylid formation. The reaction gave a mixture of *E/Z* isomers **177** in 70% yield and the stilbene **178** in 7% yield. The *Z/E* ratio of the isomers was determined as 1 to 2 according to the 2-H proton

coupling constants ($^3J_{trans}$ = 15.5 Hz, $^3J_{cis}$ = 8.0 Hz) and integral intensity of the ^{1}H NMR spectrum. Separation of the isomers by chromatography failed and sublimation at 80 °C/ 0.08 mbar yielded only *trans*-**177** with a remaining black residue inside the sublimation flask, probably formed by decomposition of the *cis*-isomer. The yellow, fluorescent *trans*-isomer was stable and could be kept without inert gas protection for several weeks at room temperature.



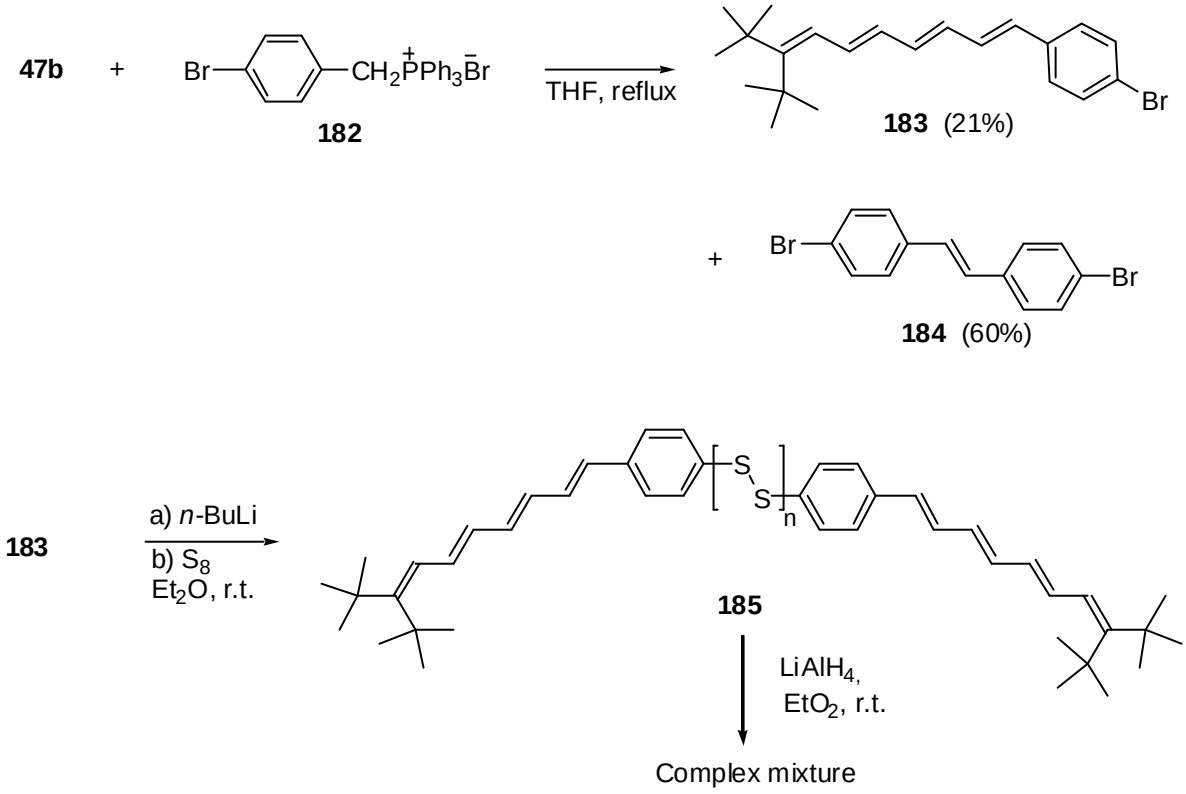
It was shown by Grahn and co-workers that aromatic bromides such as **179** can be converted to thiols by first reacting the bromide with *n*-butyl lithium, and then trapping the intermediates with elemental sufur to disulfide. The then formed **180** could be reduced with lithium aluminum hydride in 47 % overall yield[70] (Scheme 38).



Scheme 38. Conversion of aromatic bromides to thiols.

To apply this reaction to polyenes first a Wittig reaction of the aldehyde **47b** with the commercially available *p*-bromobenzyltriphenyl phosphoniumbromide **182** was carried out which yielded the corresponding bromo compound **183** in very low yield (21%).

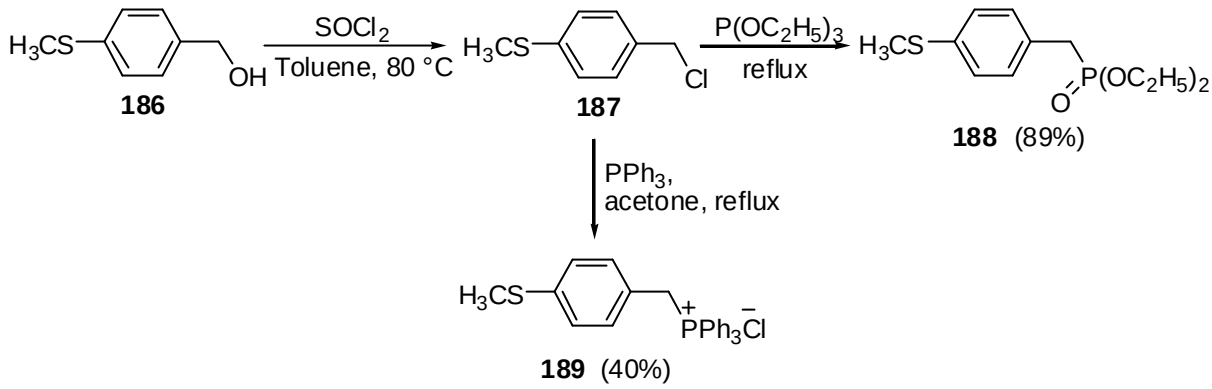
Under optimized conditions the Wittig salt **182** and the aldehyde **47b** were mixed in dry THF at room temperature and to this mixture *t*-BuOK was added slowly. When the base addition was complete the mixture was refluxed for two hours (Exp. 4.3.40). Under these conditions the desired **183** was produced in 21% yield as a single isomer (*E*-**183**). Besides, dibromostilbene **184** was formed in 60% yield as the major product. The bromo compound **183** was then treated with *n*-butyl lithium at room temperature and after 1.5 hour of stirring elemental sulfur was added to the mixture (Exp. 4.3.41). The subsequent reduction reaction of the compound, supposed to be **185**, with lithium aluminum hydride at 0 °C resulted in a complex product mixture which could not be separated.



The low yield of the Wittig reaction step and at the end the failure to purify the crude mixture made it necessary to find a new synthesis for the thiol-group functionalized polyenes.

It is possible to reduce thioethers to thiols by the use of NaH/diethylamine in HMPA, Na in liquid NH_3, etc.[68c] It is furthermore known from the literature that thioethers can be used for SAM formation. To prepare a thioether-functionalized polyene system the known phosphonate ester **188** and also the Wittig salt **189** were prepared. The first step

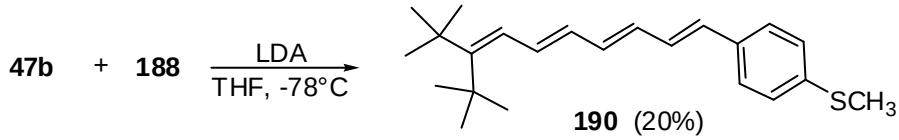
consisted in the conversion of 4-(mercaptomethyl)-benzylalcohol **186** to the benzylchloride **187** with $SOCl_2$.[71] The reaction was carried out in dry toluene at 80 °C and gave **187** in 97% yield (Exp. 4.3.42). Refluxing **187** with triethylphosphite furnished the phosphonate **188** in 89% yield (Exp. 4.3.43).[71] **187** was also reacted with triphenylphosphine in refluxing acetone providing the phosphonium salt **189** in 40% yield (Exp. 4.3.44).



186 **187** **188** (89%)

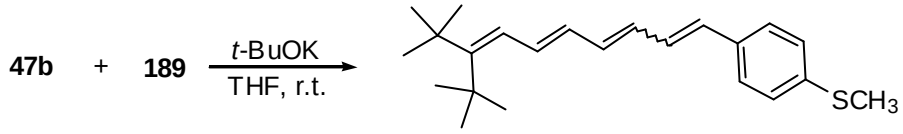
189 (40%)

Horner-Emmons reaction of **47b** with the phosphonate **188** using LDA, in THF at –78 °C finally led to the desired thioether-polyene **190** in 20% yield as single isomer, *E*-**190** (Exp. 4.3.45a).



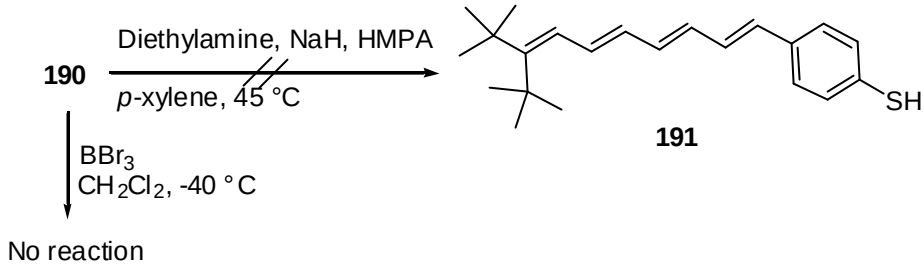
190 (20%)

The Wittig reaction of the same aldehyde with the phosphonium salt **189** using *t*-BuOK, at room temperature gave a *E/Z* mixture (ratio: 19:1), in a total yield of 64% (Exp. 4.3.45b). The isomer ratio was determined by the ^{1}H NMR analysis of the crude mixture. Separation of the isomers was performed by chromatography on silica gel with ethylacetate/hexane (1:5). The very low amount of the *Z*-isomer isolated (> 5mg) made it impossible to characterize it fully. All-*trans* **190** is a yellow solid, the UV/Vis spectra of which show a resolved vibrational fine structure. The complete spectroscopic data are collected in the experimental section (Exp. 4.3.45).

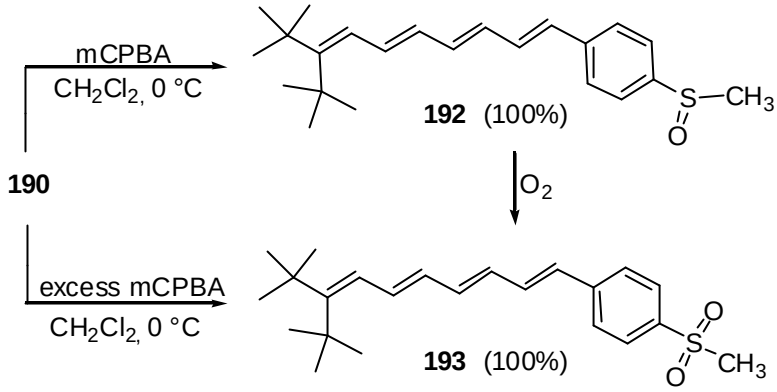


190 (64%, *cis*/*trans*, 1:19)

The reduction of the thioether **190** was tried by two different methods. In the first one **190** was heated with sodium hydride and HMPA in *p*-xylene at 45 °C in the presence of diethylamine. After work up 50% of the starting material **190** was recovered besides an insoluble, unidentified product. In the other **190** was reacted with BBr_3 in CH_2Cl_2 at –40 °C. After work up, the starting material was completely recovered. Because of the presence of double bonds harder reduction conditions such as reduction with Na in liquid ammonia were not tried.

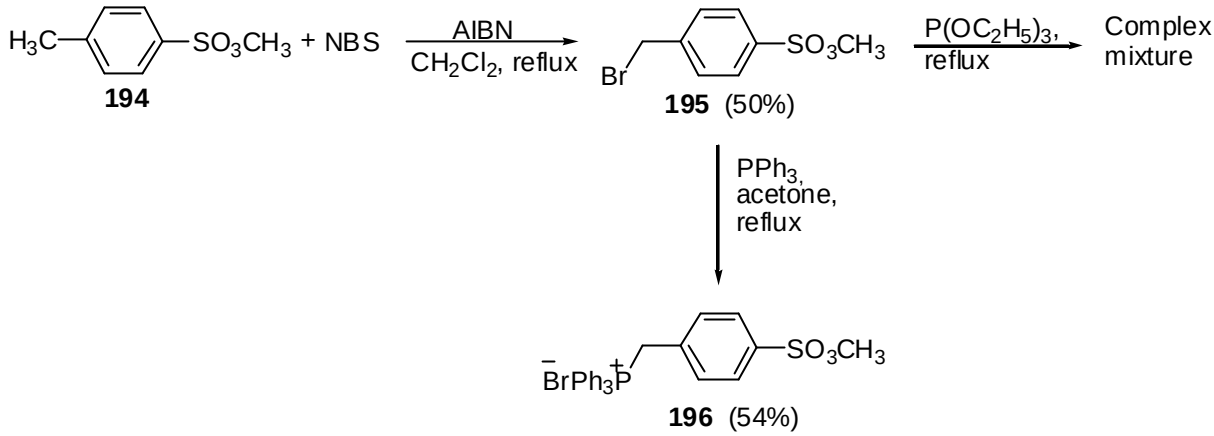


To test the reactivity of **190** two more reactions were carried out. Oxidation of **190** with 1 equivalent of MCPBA (*meta*-chloroperbenzoic acid) to prepare the sulfoxide **192**, and reaction with excess MCPBA to prepare the sulfone **193**. Both reactions took place quantitatively within minutes (Exp. 4.3.46, 47). Both compounds are bright yellow solids with absorption maxima at 360 nm (**192**) and 366 nm (**193**). While the spectra of **192** was partly resolved, **193** gave a broad absorption band. As can be expected the sulfoxide **192** is very sensitive to air and forms the sulfone **193** readily. But under N_2 gas it could be kept for several weeks. The sulfone **193** is stable even without inert gas protection at room temperature.

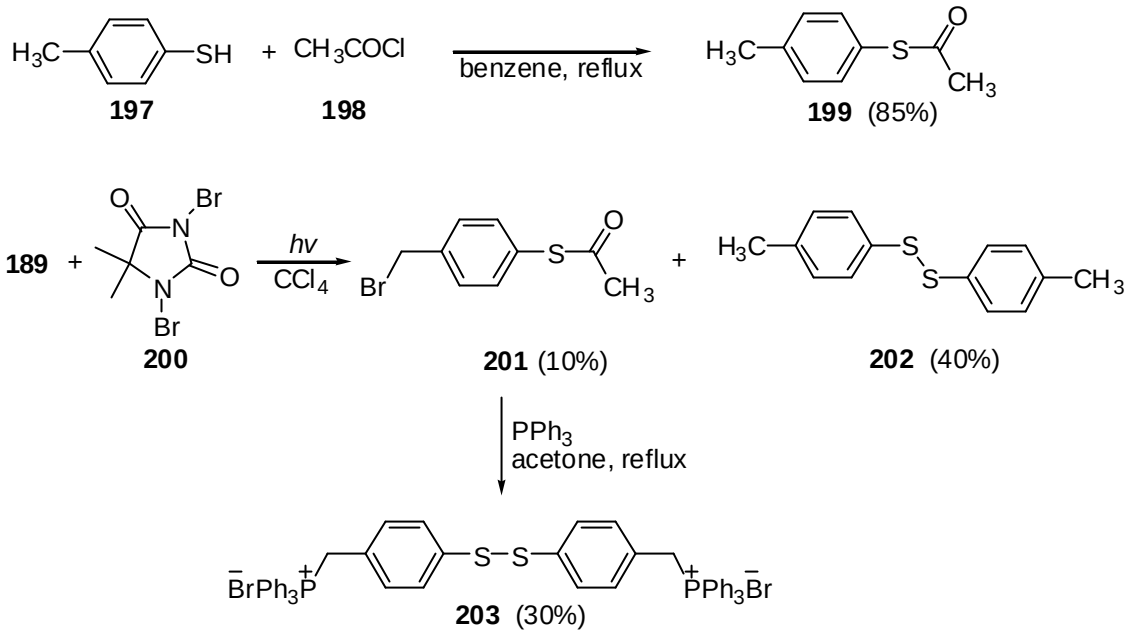


Thiols can also be prepared by the reduction of sulfonic acid esters. For the preparation of a thioester-functionalized polyene, *p*-toluenesulfonic acid methylester **194** was chosen as the starting material. The benzylic postion was brominated with *N*-bromosuccinimide. [72] The highest yield (50%) was obtained when 1 equivalent of the ester **194** was reacted with 1.6 equivalents of NBS in refluxing CCl_4, in the presence of a catalytical amount of AIBN (Exp. 4.3.48). The bromo product **195** was then reacted with an equimolar amount of triphenyl phosphine in refluxing acetone providing the Wittig salt **196** in 54% yield (Exp. 4.3.49). However, the salt **196** turned out to be completely insoluble in the common organic solvents and H_2O so that it was impossible to carry out a satistfactory Wittig reaction with the aldehyde **47b**.

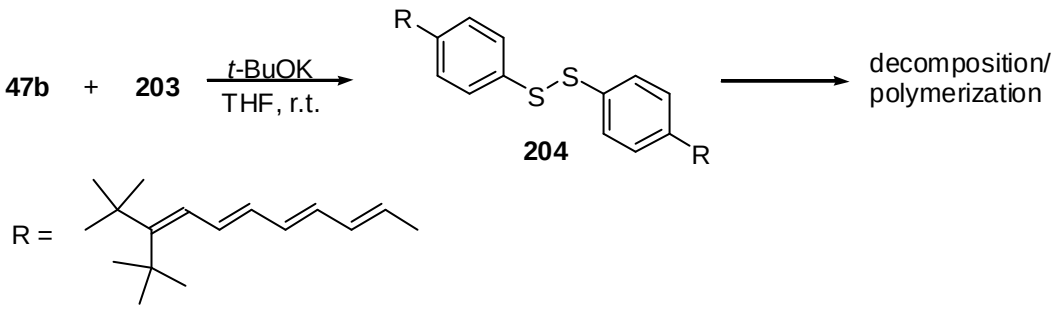
An Arbuzov reaction between triethylphospite and **195** to prepare the corresponding phosphonate failed, probably due to the fact that the ester group of the sulfonic acid ester is a very good leaving group which competes with bromine during the course of the reaction. The reaction between **195** and triethyl phosphite gave a complicated crude mixture which could not be purified or characterized.



Thiols can easily be protected by benzoyl or acetyl groups and at the end of a reaction sequence deprotection requires very mild conditions only such as stirring in an aqueous solution of an inorganic base.[68c] The last reaction sequence that was carried out to prepare a thiol-functionalized polyene started by protection of *p*-thiocresol (**197**) with acetylchloride (**198**).[73] Refluxing an equimolar amount of the two compounds in benzene yielded 85% of the protected thiol **199** (Exp. 4.3.50). The next step consisted in the bromination of the benzylic postion. It should be mentioned that the protection of the thiol is obligatory before the bromination reaction, because in the literature *p*-bromobenzylthiocresol has been reported as a very unstable compound.[74] The bromination reaction of **199** by NBS gave a very complex product mixture; therefore the reagent was changed to 5,5-dimethyl-*N*,*N*-dibromohydantoin (**200**), a brominating agent known to be milder. Under optimized conditions the reaction was carried out by using 1 equivalent of **199** and 0.5 equivalent of **200** in carbontetrachloride. An Osram 300 Watt sun lamp was used to initiate the radical formation. The reaction gave only 10 % of the brominated compound **201**, 40% of disulfide **202** being formed as the major product (Exp. 4.3.51). The bromo derivative **201** was reacted further with triphenlyphosphine both in refluxing toluene and acetone, yielding the bis Wittig salt **203**. The solvents, acetone or toluene, had no influence on the yield, it remained around 30% (Exp. 4.3.52).



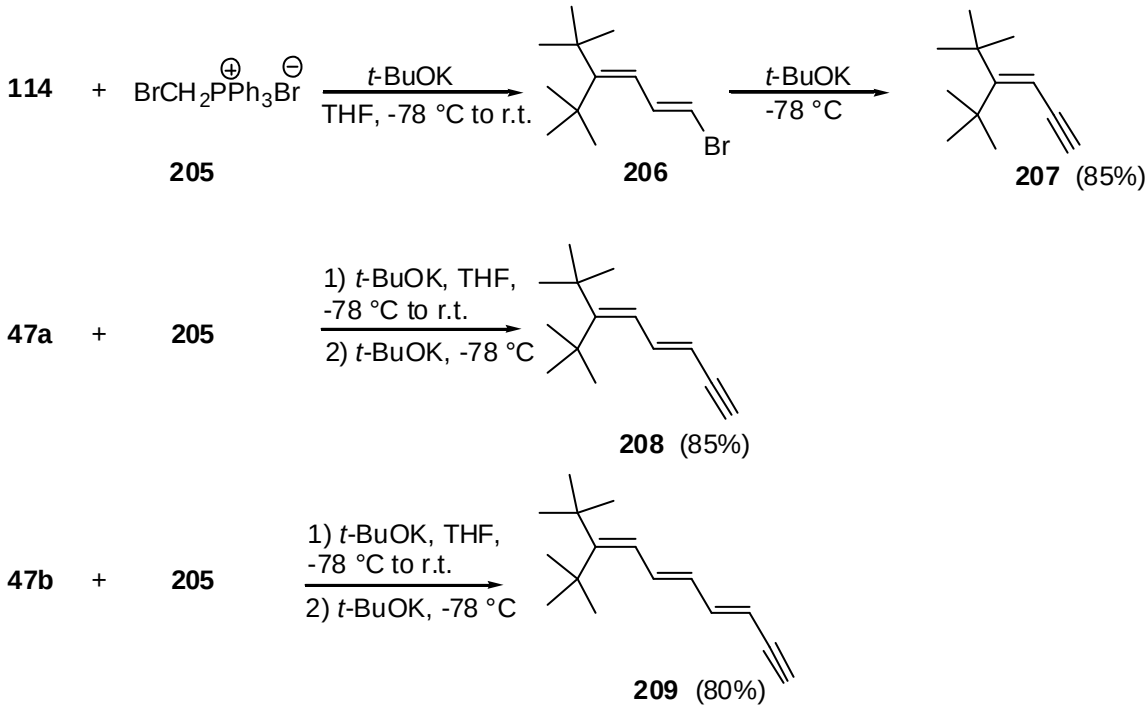
The reaction of the aldehyde **47b** with the bis Wittig salt **203** in the presence of *t*-BuOK in THF at room temperature gave the desired disulfide **204** (probably as an isomer mixture) as indicated by the ^{1}H NMR spectra of the crude product (Exp. 4.3.53). However, the compound was very unstable and decomposed or polymerized very quickly and could hence not be purified and characterized completely.



2.5. Polyeneynes

2.5.1. Terminal acetylenes

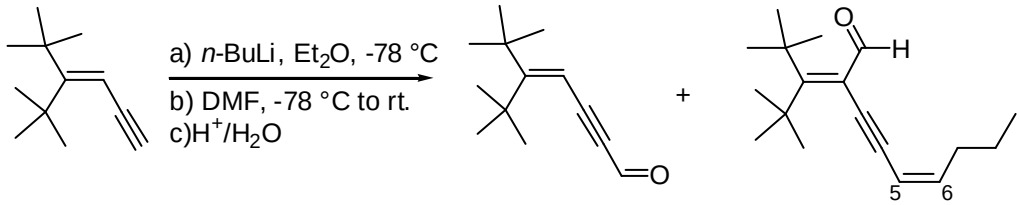
Terminal acetylenes can be very conveniently prepared from aldehydes by a one-pot synthesis.[75] The first step involves a Wittig reaction between the aldehyde and a bromoalkyl-phosphorane which is followed by dehydrobromination by excess base. In the present work the terminal acetylenes **207**, **208** and **209** were all prepared using this reaction sequence. The reactions started with the generation of bromomethyl triphenlyphosphorane by the addition of equimolar amount of *t*-BuOK to the Wittig salt **205** in THF at –78 °C. The colour change from colourless to yellow-orange indicated the formation of the ylid and after a short time the necessary aldehyde (**114**, **116a**, **116b**) was added dropwise to the mixture. The conversion of the starting material to bromoalkene **206** was over when the reaction reached room temperature. The mixture was then cooled back to –78 °C and treatment with excess *t*-BuOK led to the elimination furnishing the terminal acetylenes **207**, **208, 209** in high yields (Exp. 4.3.54 - 56).



The smallest acetylene **207** is a volatile colourless oil and its purification was carried out by chromatography on silica gel with pentane. The second acetylene, **208**, is also a colourless oil but not as volatile as the first one. It could be purified easily by silica gel chromatography by using higher boiling non-polar solvents like hexane. The third and last member of the series, **209**, is a light yellow oil at room temperature and a solid below 0 °C which could again be purifed on silica gel either with pentane or hexane. The hydrocarbons **207** and **208** are quite stable for several weeks when kept under inert atmosphere and in the cold, but exposure to air or leaving them at room temperature was observed to cause polymerization. The longest terminal acetylene **209** was less stable even in the cold and under inert atmosphere and polymerized in a few days. The shift in the absorption maxima on going from **207** to **209** is similar to that observed for the polyenes as will be discussed in section 2.6.

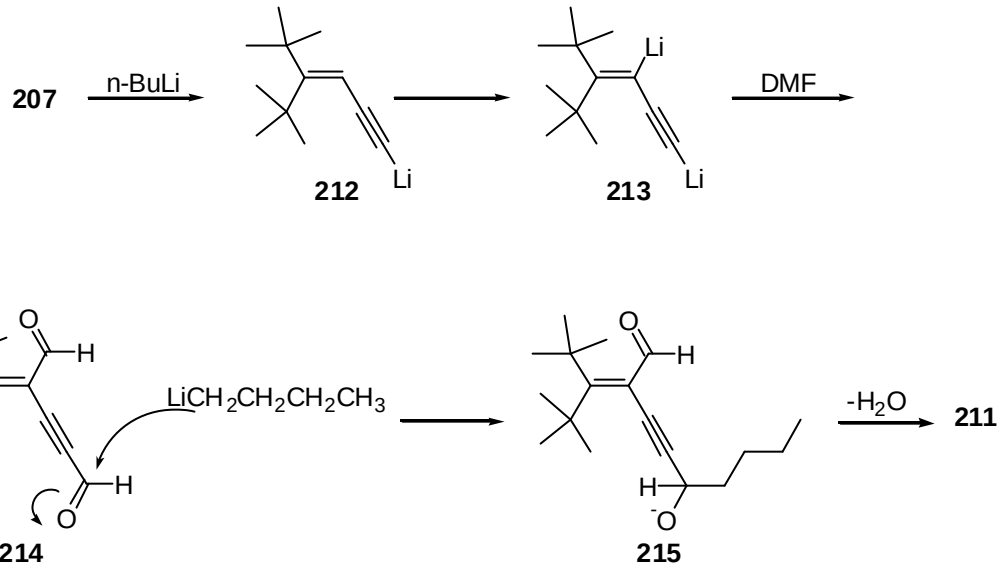
2.5.2 Preparation of the ynal 210 and the enediyne 121

Terminal acetylenes can be converted to acetylenic aldehydes by first reacting the acetylene with butyl lithium and then reacting the lithiumacetylide with dimethylformamide (DMF) or formaldeyhde.[76] When DMF is used hydrolysis with aqueous acid gives the aldehyde readily, whereas with formaldehyde, because the resulting compound is an alcohol, one further oxidation step is necessary. Treating **207** with 1.6 equivalents of *n*-BuLi in dry Et_2O at −78 °C gave the lithiumacetylide, the formation of which was easily observed by the dramatic colour change of the solution from colourless to deep red during the addition of the base. At the same temperature DMF was added and after the reaction had reached room temperature work up gave **210** in 85 % and the side product **211** in 10 % yield (Exp. 4.3.57). Purification of the product was performed on silica gel with pentane as the eluent. The aldehyde **210** is a red oil and quite stable as long as it is kept at low temperatures.

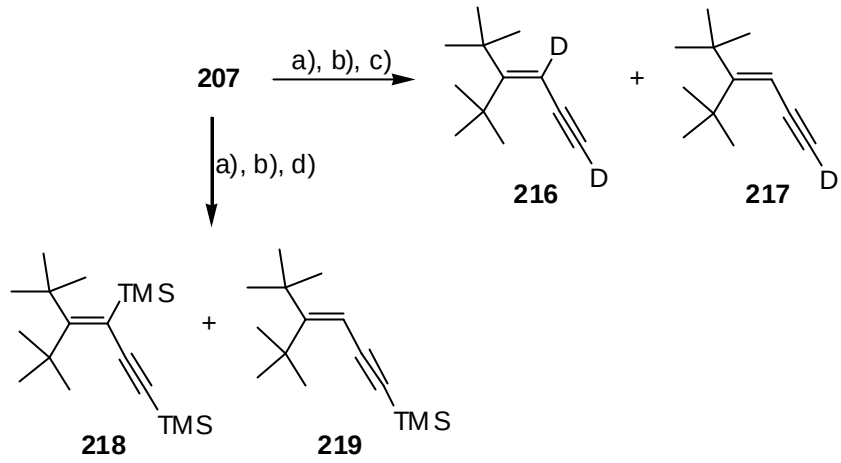


207 **210** (85%) **211** (10%)

The formation of the side product **211** can be explained by dimetallation of **207** to **213** by *n*-BuLi treatment. Dimetallation of 1-butene-3-yne under strongly basic conditions (BuLi/*t*-BuOK) has been investigated by Brandsma et al.[77] After the dimetallation formylation at both sides evidently takes place, leading to **214**. This is finally attacked by excess *n*-BuLi to provide - via **215** and dehydration - the observed aldehyde **211**. The C5-C6 bond of **211** was found to posses a *cis*-configuration according to the ^{1}H NMR coupling constant (^{3}J = 3 Hz).

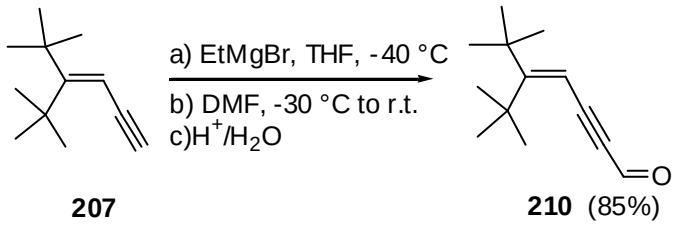


To prove that the dimetallation hypothesis was correct, two trapping experiments with D_2O and TMSCl were carried out. After the lithiation of **207** by *n*-BuLi (Exp. 4.3.57) the reaction mixture was divided into two halves. The first half was quenched with two equivalents of D_2O at –78 °C. The formation of a white precipitate was observed and the reaction was left to warm up room temperature. The precipitate was removed by filtration and after removal of solvent GC/MS analysis of the crude product showed the presence of di-deuterated compound **216** (*m*/*z*: 166 [M^+]) besides the mono-deuterated **217** (*m*/*z*: 165 [M^+]). The other half of the reaction mixture was cooled to 0 °C and this time two equivalents of TMSCl were added, the colour of the solution turned from red to white. After work-up GC/MS analysis of the crude product showed the formation of both di- **218** (*m*/*z*: 294 [M^+-CH_3]) and mono- **219** (*m*/*z*: 235 [M^+-H]) sillilated compounds.



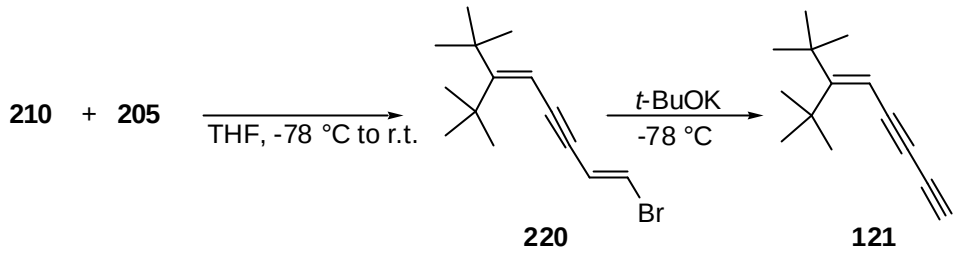
(a) n-BuLi, Et_2O, -78 °C; (b) DMF, -78 °C; (c) D_2O, -78 °C; (d) TMSCl, 0 °C

The aldehyde **210** was obtained as the only product when, instead of *n*-BuLi, freshly prepared EtMgBr was used for metallation. To a solution of **207** in THF cooled to –40 °C, 1.2 equivalents of EtMgBr were added slowly. During the addition initially the formation of a white, then grey suspension was noted. The reaction was left to warm up to room temperature followed by an additional 1 hour stirring. After addition of DMF and work-up **210** was obtained in 85% yield (Exp. 4.3.57).



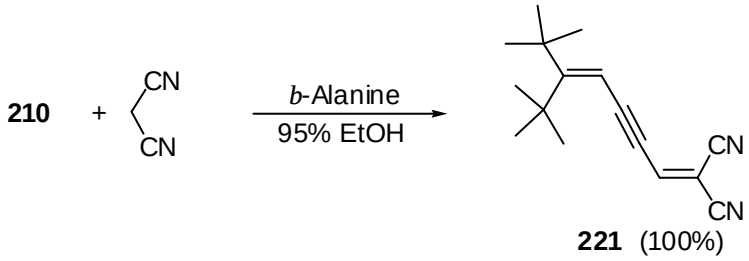
The Wittig reaction of the aldehyde **210** with bromomethyltriphenlyphosphorane, generated at –78 °C by the addition *t*-BuOK to bromomethyltriphenly-phosphoniumbromide **205**, as explained before, resulted in the formation of the bromo derivative **220**. Compound **220** was not isolated but subjected to dehydrobromination by excess base giving the product **121** (Exp. 4.3.60). The enediyne **121** is very unstable and trying to purify the crude product resulted in polymerization only. For this reason the characterization of the compound had to be carried out by using the crude mixture.

Because of its instability, the hydrocarbon had to be used as formed; the coupling reactions of the terminal acetylenes are discussed in Section 2.5.

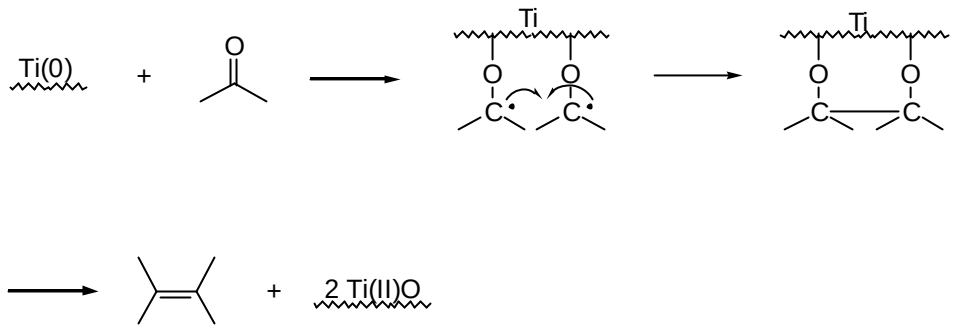


2.5.3 Knoevenagel and McMurry reactions of the aldehyde 210

With the acetylene aldehyde **210** two more reactions were performed. First its Knoevenagel condensation with malononitrile was carried out in 95 % EtOH in the presence of a catalytical amount of *b*-alanine (Exp. 4.3.58). After chromatographic purification on silica gel **221** was obtained in quantitative yield as a greenish-yellow oil. In the UV/Vis spectrum **221** absorbed at 362 nm, quite close to the absorption maximum of the dicyanopolyene **161** (3 double bonds) at 374 nm.

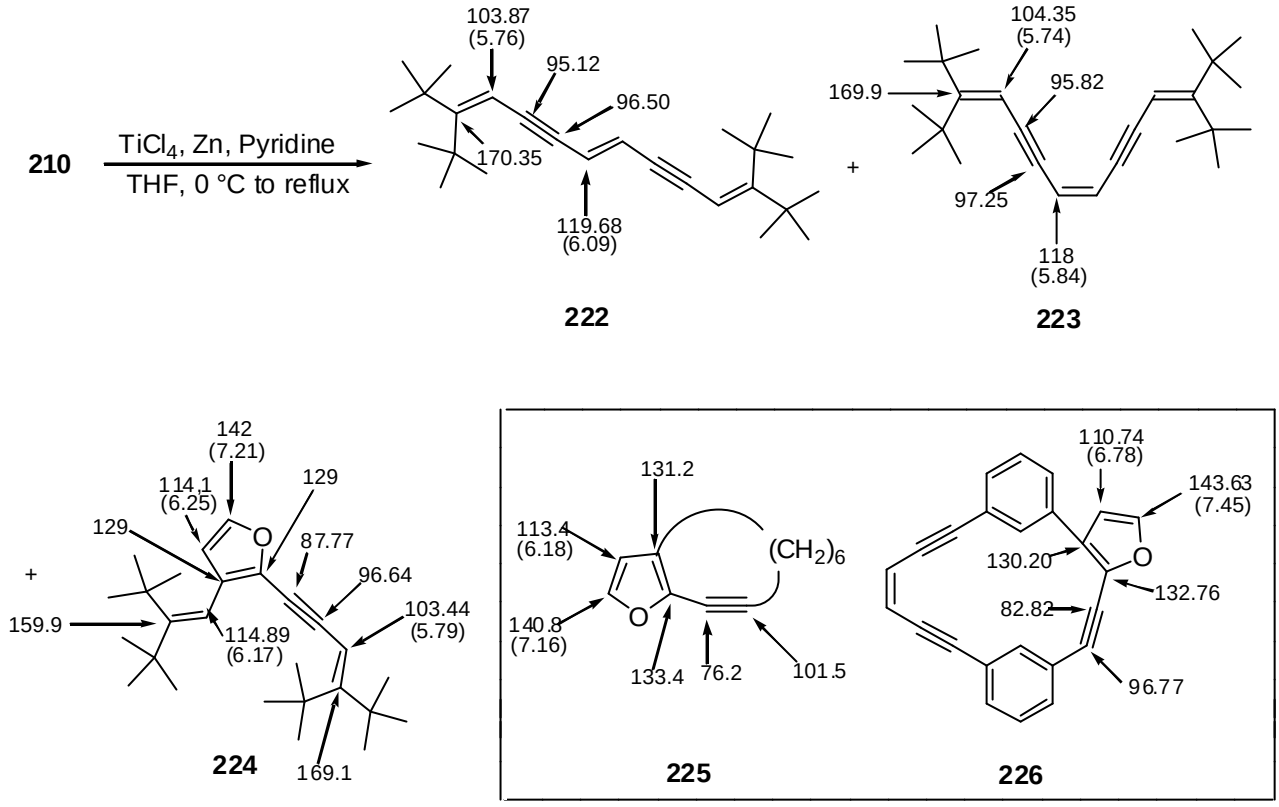


A very convenient and widely used method to prepare symmetrical polyenes and/or polyenyne systems is the McMurry coupling reaction, in which two aldehydes or ketones are connected in the presence of a Ti(0) catalyst.[78] The catalyst is prepared in situ by the reduction of $TiCl_3$ or $TiCl_4$ by zinc or magnesium. Although uncertainities still exist concerning the mechanism of the reaction, it is supposed to take place via ketyl radicals that form by reduction of the carbonyl group. The ketly radical is then assumed to attach itself to the Ti(0) surface, followed by the dimerisation of two radicals and breaking of the carbon-oxygen bond finally giving the olefin and Ti(II)O.



Scheme 37. Mechanism of the McMurry reaction.

The McMurry coupling reaction of **210** was performed using $TiCl_4$ (Exp. 4.3.59). First this chloride was reduced to Ti(0) by Zn in the presence of pyridine in THF at 0 °C. To this mixture the aldehyde **210** was then added at 0 °C, cooling was removed and reflux started. When the starting material had been consumed completely three products were formed. Purification by column chromatography on silica gel yielded the *trans*-**222** in pure form. However, it was not possible to separate the other two products from each other by various separation techniques, including column chromatography on silica gel, with silver, and sublimation. The overall yield of the reaction was 70% with a ratio of 3:1:1 according to peak intensities in the ^{1}H NMR spectra, the main product being *trans*-**222**. One of the inseparable products is very likely the *cis*-isomer **223** according to NMR and GC/MS results (see Exp. 4.3.59). The third product was tentatively identified as the furan derivative **224**. A similiar furan formation in McMurry coupling reactions of acetylenic aldehydes were reported by Krüger and Srinivasan.[79] All NMR signals of the furan derivative are in accordance with the referance compounds **225** and **226** as summarized in Scheme 39. Values given in parantheses refer to the ^{1}H NMR results.



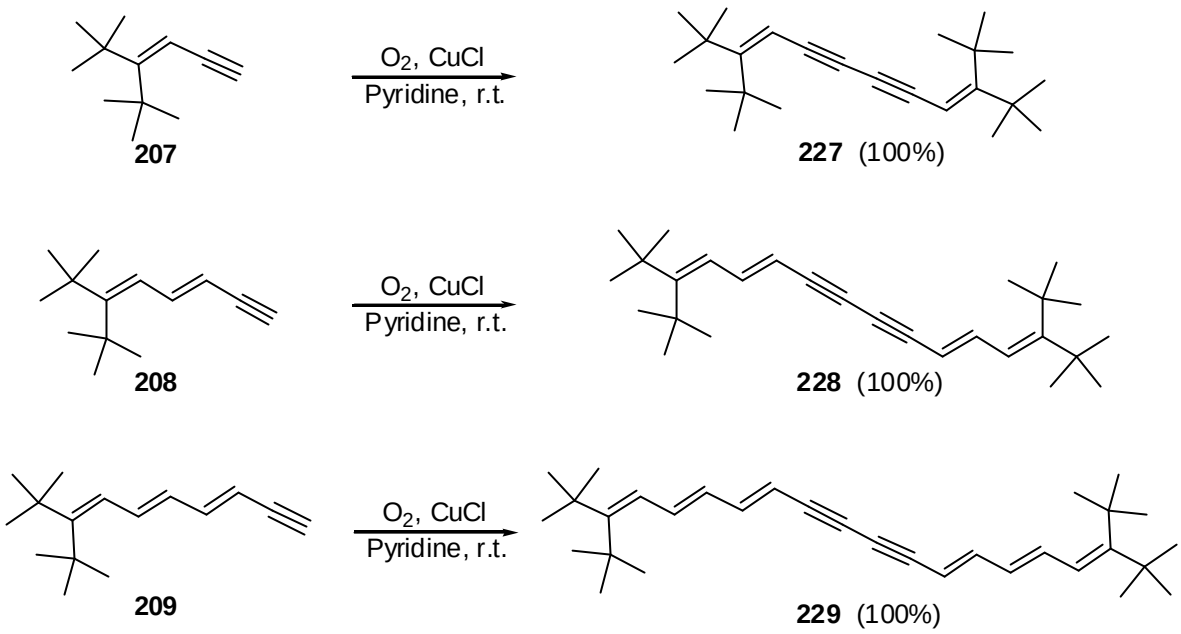
Scheme 39. ^{1}H and ^{13}C NMR data of **222**-**224** as well as of the reference compounds **225** and **226**.[79]

2.5.4 Oxidative coupling reactions of terminal acetylenes

2.5.4.a Tetra-*tert*-butyl substituted diacetylenes 227, 228 and 229

In the first chapter it was mentioned that oxidative homo- and cross-coupling between the *sp*-carbon centers of terminal alkynes is one of the most useful synthetic methods to prepare polyacetylenes (Sec. 1.2). In this study the di-*tert*-butyl substituted terminal acetylenes **207**, **208** and **209** (Sec. 2.5.1.) were all dimerized by Glaser coupling under typical Hay conditions. In all three reactions oxygen gas was passed through a mixture of 1 equivalent of the terminal acetylene and 0.3 equivalent of CuCl in pyridine for two hours (Exp. 4.3.61 - 63). The purification of the first two diacetylenes **227** and **228** was carried out by sublimation at 75 °C/ 4 mbar and 120 °C/ 4 mbar, respectively. The longest member **229** was purified by chromatography on silica gel with pentane. All diacetylenes were formed in quantitative yield. The smallest diacetylene **227** is colourless and the

other two, **228**, **229**, are yellow solids. All compounds are highly stable and they are resistent both towards air/oxygen and high temperature; even after melting no decompositon was observed. Their UV/Vis absorption spectra are discussed in Sec. 2.6.



The recrystallization of all three compounds from EtOH gave crystals suitable for X-ray structure analyses. Structures of **227, 228** and **229** are given in Fig. 12, 13 and 14 respectively. Table 4 shows the C-C bond lengths and Table 5 shows the angles between the carbon atoms of the chain.

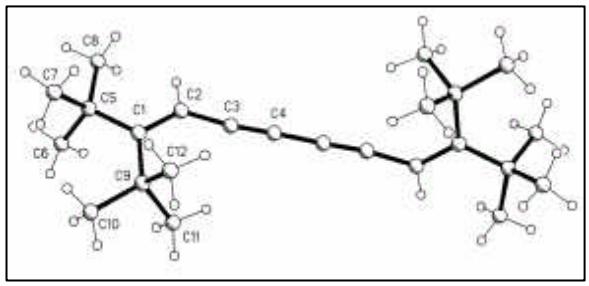


Figure 12. Structure of **227** in the crystal.

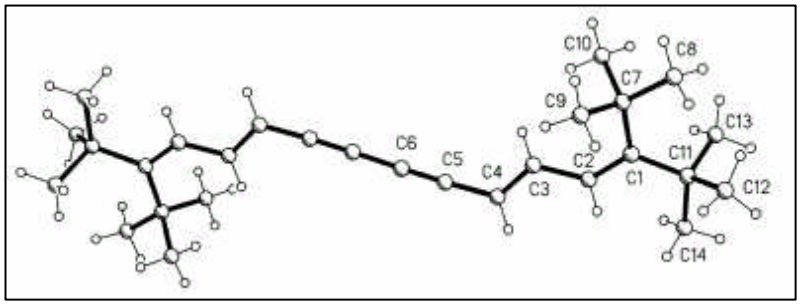


Figure 13. Structure of **228** in the crystal.

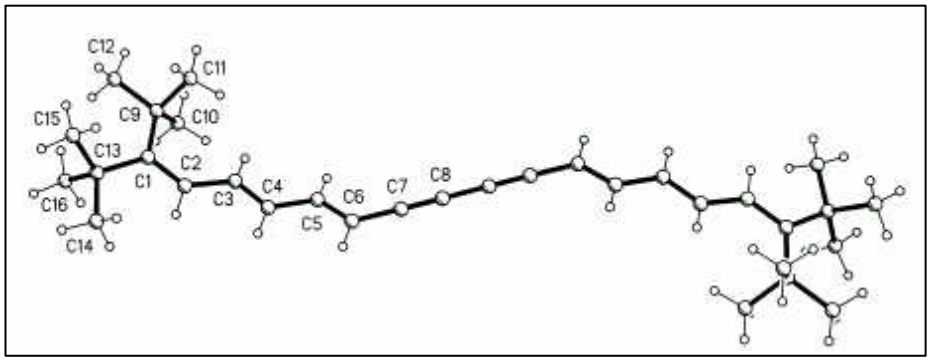
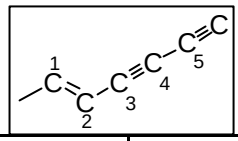


Figure 14. Structure of **229** in the crystal.

	C1- C2	C2- C3	C3- C4	C4- C5	C5- C6	C6- C7	≡	↓≡
227	135.44	142.30	≡→				120.59	137.30
228	135.49	145.17	134.41	141.85	≡→		120.91	136.80
229	135.10	145.10	134.10	143.30	133.7	141.5	120.80	136.90

Table 4. Bond lengths (pm) of the diacetylenes **227 - 229**.

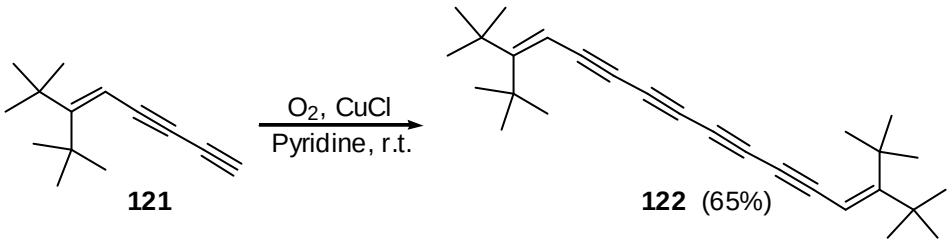


	C1-C2-C3	C2-C3-C4	C3-C4-C5
227	129.25	172.95	177.56
228	122.87	177.96	178.80
229	125.21	176.50	179.20

Table 5. Bond angles (°) of the diacetylenes **227 - 229.**

2.5.4.b Tetra-*tert*-butyl substituted tetraacetylene 122

The above oxidative coupling reaction was also applied to the enediyne **121** and the highly stable tetraacetylene derivative **122** was obtained in 65 % yield as a yellow solid (Exp. 4.3.64). Its UV/Vis absorption properties will also be discussed on the following page (Sec. 2.6).



Recrystallization of **122** from EtOH gave crystals suitable for its X-ray structure analysis (Fig. 15). As can be seen from the crystal packing diagram of the compound **122** (Fig. 16) the close approach of the molecules toward each other is prevented by the bulky tetra-*tert*-butyl groups, presumably one of the reason for the extreme stability of the hydrocarbon.

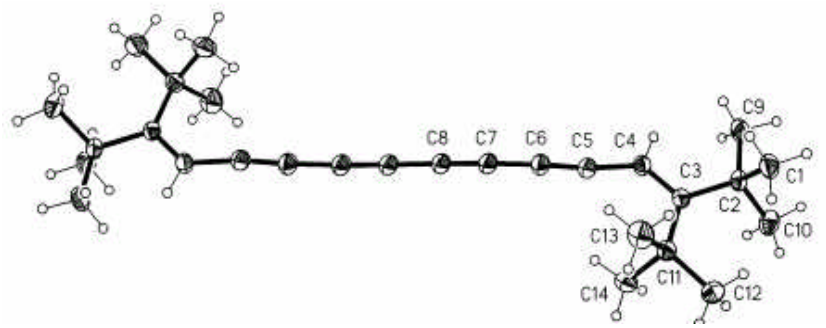


Figure 15. Structure of **122** in the crystal.

	C3-C4	C4-C5	C5-C6	C6-C7	C7-C8	C8-C8*
Bond length (A°)	1.3564	1.4188	1.2132	1.3621	1.2149	1.3551
	C3-C4-C5	C4-C5-C6	C5-C6-C7	C6-C7-C8	C7-C8-C8*	
Bond angle (°)	129.41	172.72	175.46	177.35	178.91	

Table 6. Bond lengths (Å) and bond angles (°) of **122**.

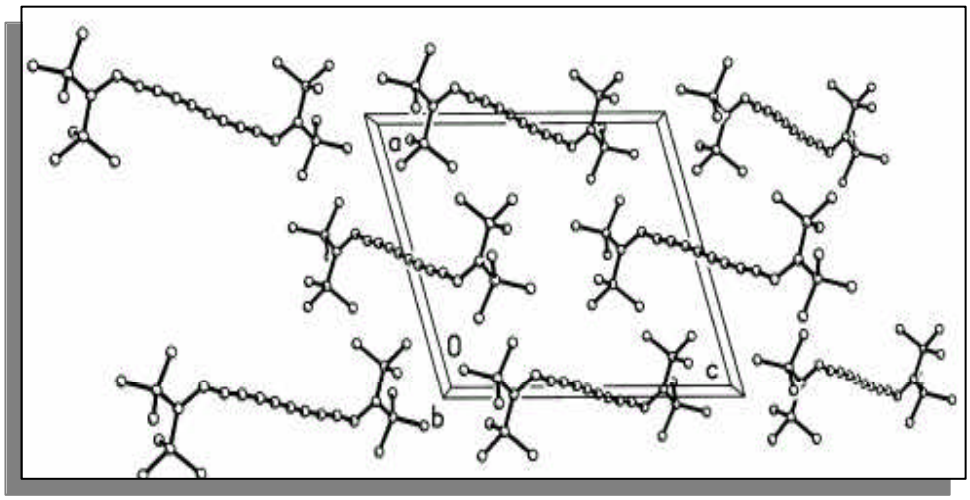


Figure 16. Crystal packing diagram of **122**. Unit cell dimensions: a = 11.4627 (14) Å, b = 8.1292 (10) Å, c = 13.4476 (18) Å; $\alpha = 90°$, $\beta = 107.906\ (3)°$, $\gamma = 90°$.

2.6 UV/Vis absorption spectra of polyacetylenes

UV/Vis spectroscopy is one of the most important methods for structure determination of di- and polyacetylenes. Their electronic spectra are usually very typical and show sharp vibrational fine structures. Normally two sets of bands due to $\pi \rightarrow \pi^*$ transitions are observed, the longer-wavelength-series of lower intensity and the shorter-wavelength-series with very high intensity.[1, 65] The tetraacetylene compound **122** shows these very characteristic properties nicely with highly intense bands at shorter wavelengths followed by weak bands at longer wavelengths. The bands are well resolved showing the vibrational fine structure (Fig.17).

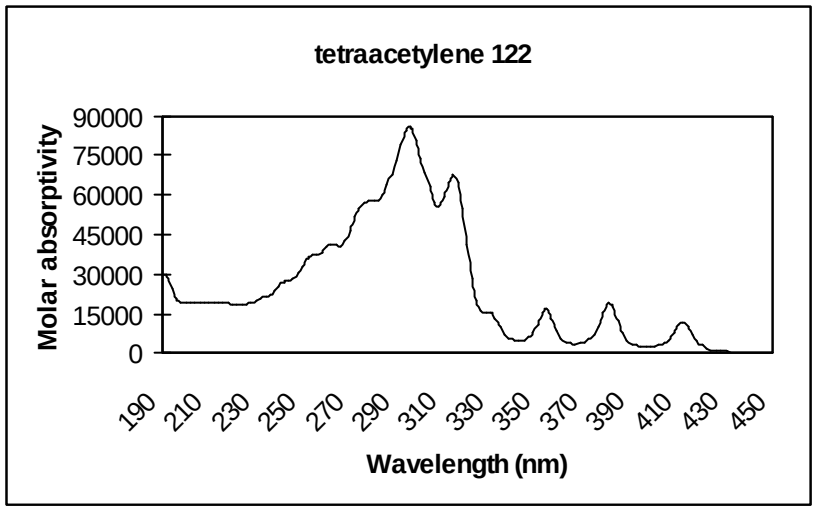


Figure 17. Absorption spectrum of tetraacetylene **122** in acetonitrile.

The diacetylene compounds **121** and **227**, where the triple bonds are in conjugation with one double bond, show similar spectra. However, the intense shorter wavelength bands were not well resolved; only the weak bands at longer wavelengths show the distinct vibronic transitions (Fig. 18 and 19).

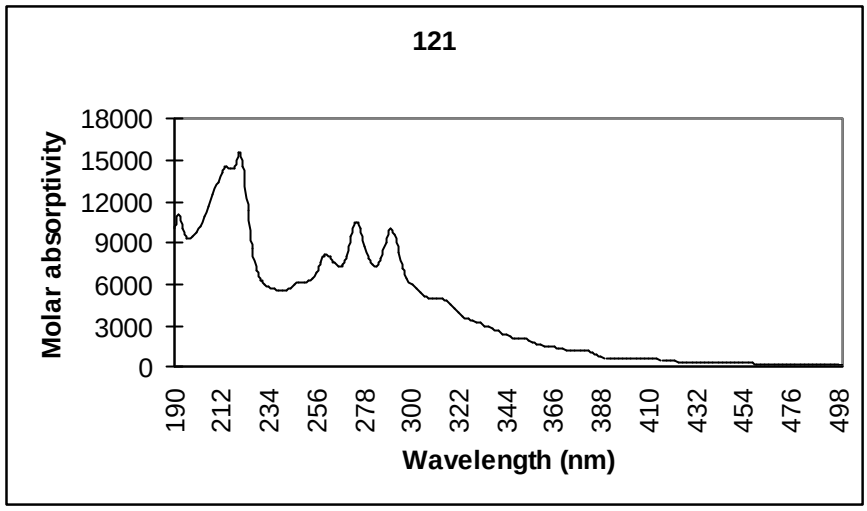


Figure 18. Absorption spectrum of endiyne **121** in acetonitrile.

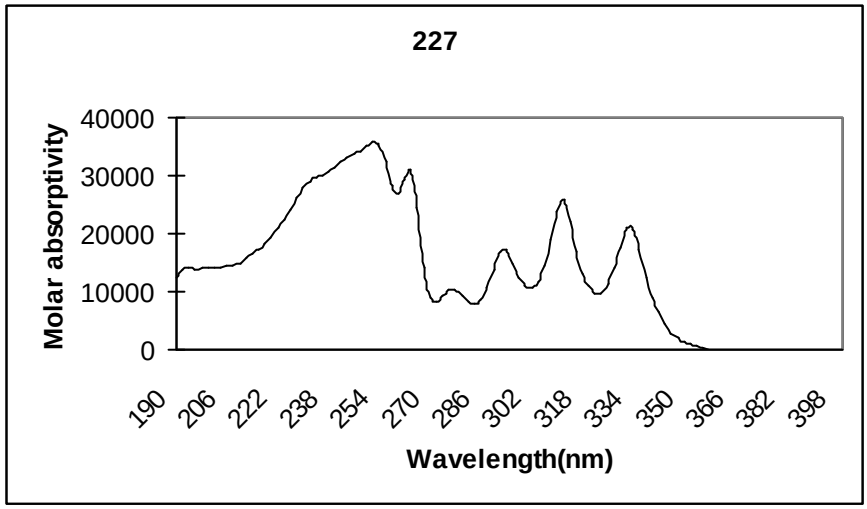


Figure 19. Absorption spectrum of diyne **227** in acetonitrile.

As the number of conjugated double bonds of the diyne hydrocarbons increases the diacetylene absorption spectra starts losing their characteristic appereance and look more like partly resolved polyene spectra. The two sets of bands at lower and higher wavelengths are not resolved well, they rather start to show very broad maxima. The bands became more intense at longer wavelengths, just the reverse of what was explained

above, but very typical for the polyenes. The increase in chain length caused the absorption maxima to shift to higher wavelengths (Fig. 20 and 21).

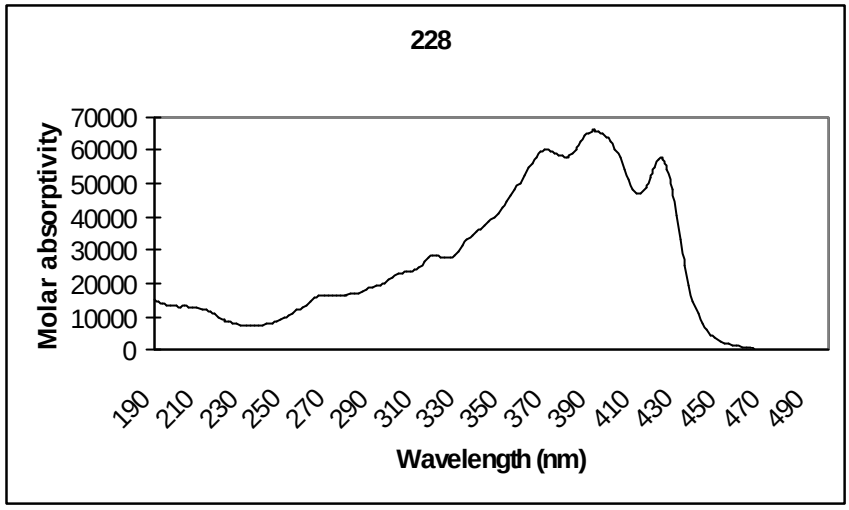


Figure 20. Absorption spectrum of diyne **228** in acetonitrile.

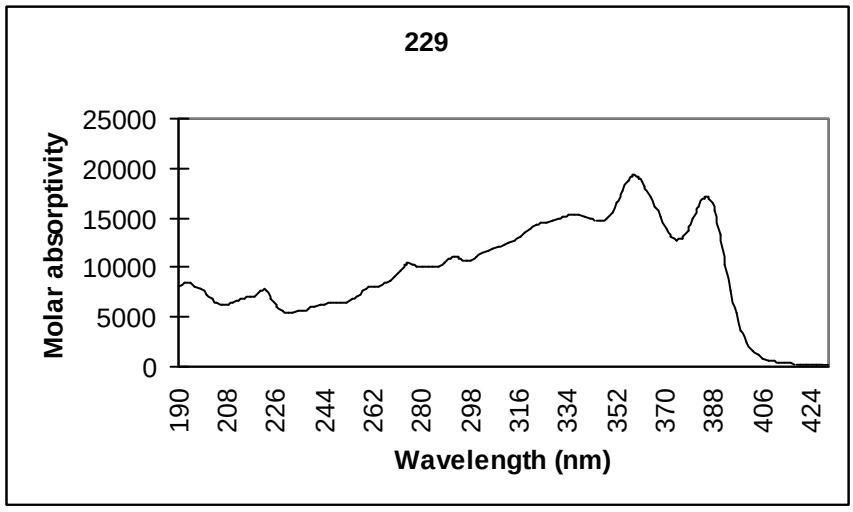
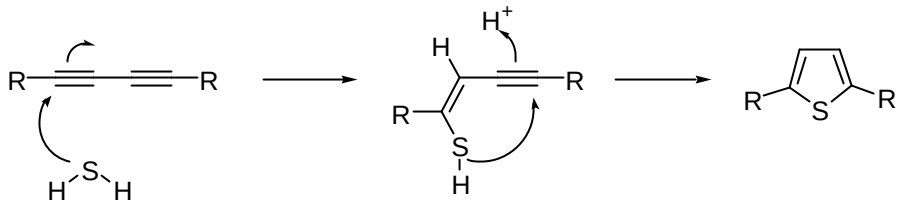


Figure 21. Absorption spectrum of diyne **229** in acetonitrile.

The absorption spectra of the terminal acetylenes **207**, **208**, **209** do not show well resolved spectra, the bands being rather broad. The absorption maximum of compound **207** was at 234 nm. Increase in chain length caused absorption to shift to higher wavelengths, and the absorption maxima for compounds **208** and **209** appeared at 276 nm and 310 nm, respectively.

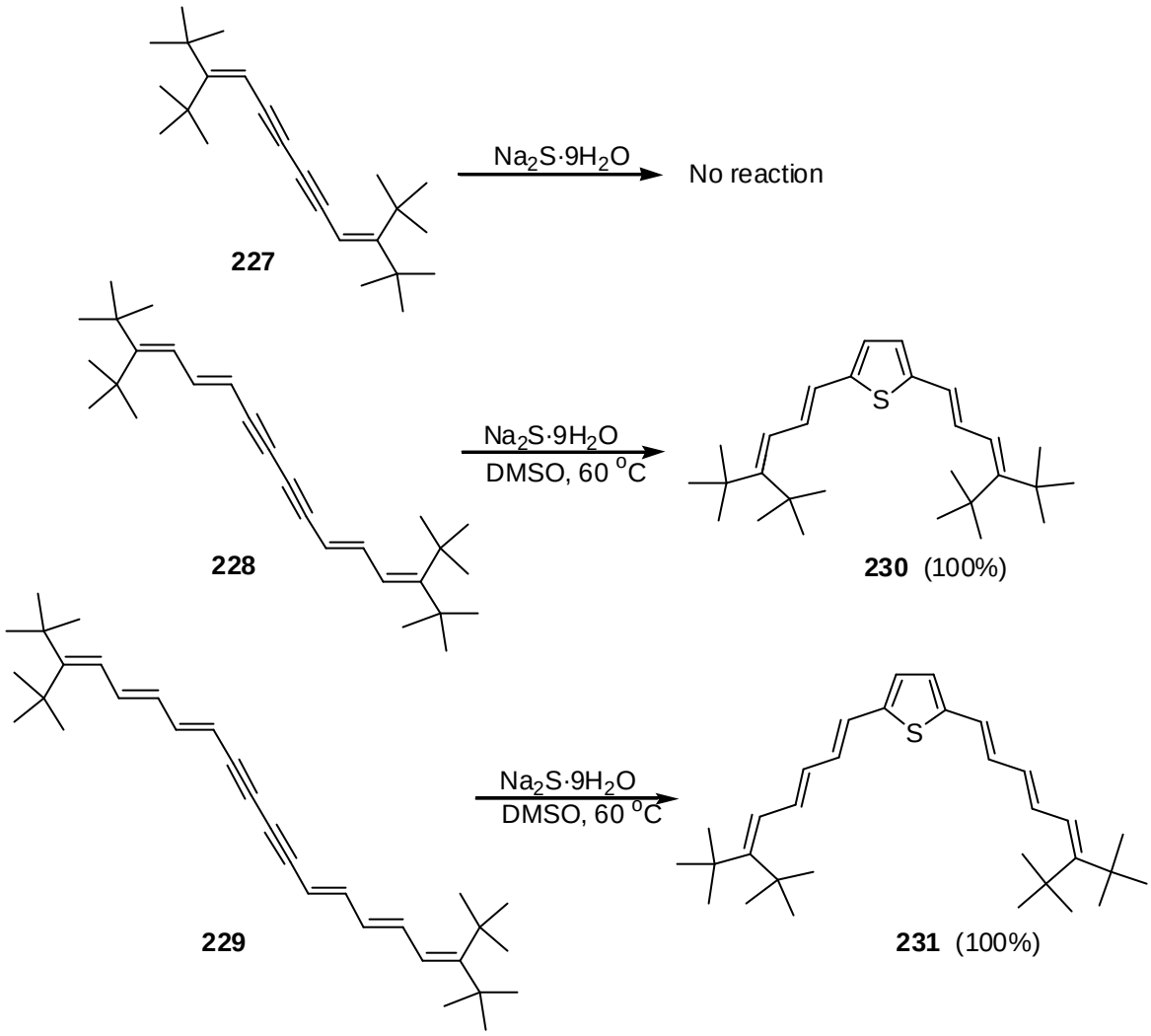
2.7 Thiophene derivatives

A common reaction in the field of natural diacetylenes is thiophene formation by the addition of hydrogen sulfide to the conjugated triple bonds. It was studied in detail by Bohlmann and co-wokers.[1] The reaction proceeds by a two step mechanism as shown in Scheme 40.

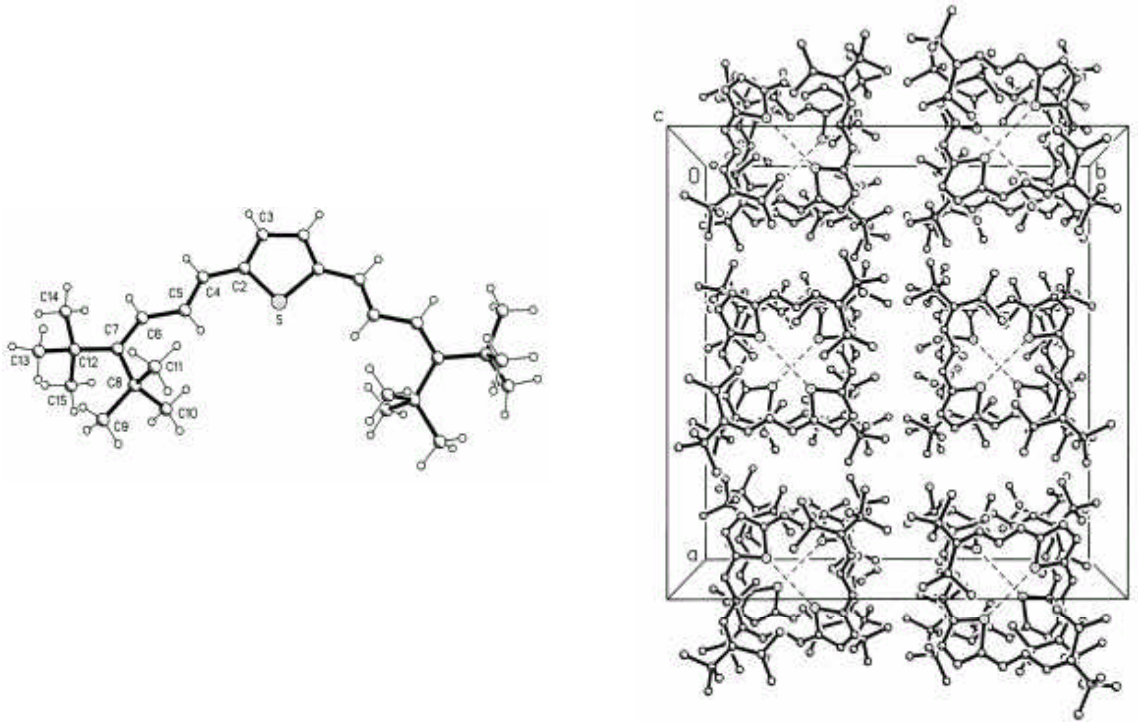


Scheme 40. Thiophene formation by addition of H_2S to the conjugated triple bonds.

The thiophene formation reaction can also be carried out with $Na_2S{\cdot}9H_2O$ instead of H_2S, a process reported in the literature to take place in very high yields.[80] The diacetylene compounds 227, 228, and 229 were therefore investigated with respect to formation of thiophene derivatives by the use of $Na_2S{\cdot}9H_2O$. In these reactions one equivalent of the diacetylene, 2.2 equivalents of $Na_2S{\cdot}9H_2O$ and 2 equivalents of KOH were mixed in dimethylsulfoxide and the mixture stirred for 20 minutes at 60°C. After work-up followed by chromatographic purification on silica gel the thiophenes 230 and 231 were obtained in quantitative yield (Exp. 4.3.65, 66). The smallest diacetylene 227, however, remained unchanged and no thiophene derivative was formed. Changing the solvent from DMSO to methanol, increased reaction times or reflux conditions also did not lead to any reaction. The unreactivity of 227 towards thiophene formation is presumably due to steric hindrance caused by the bulky tetra-*tert*-butyl groups.

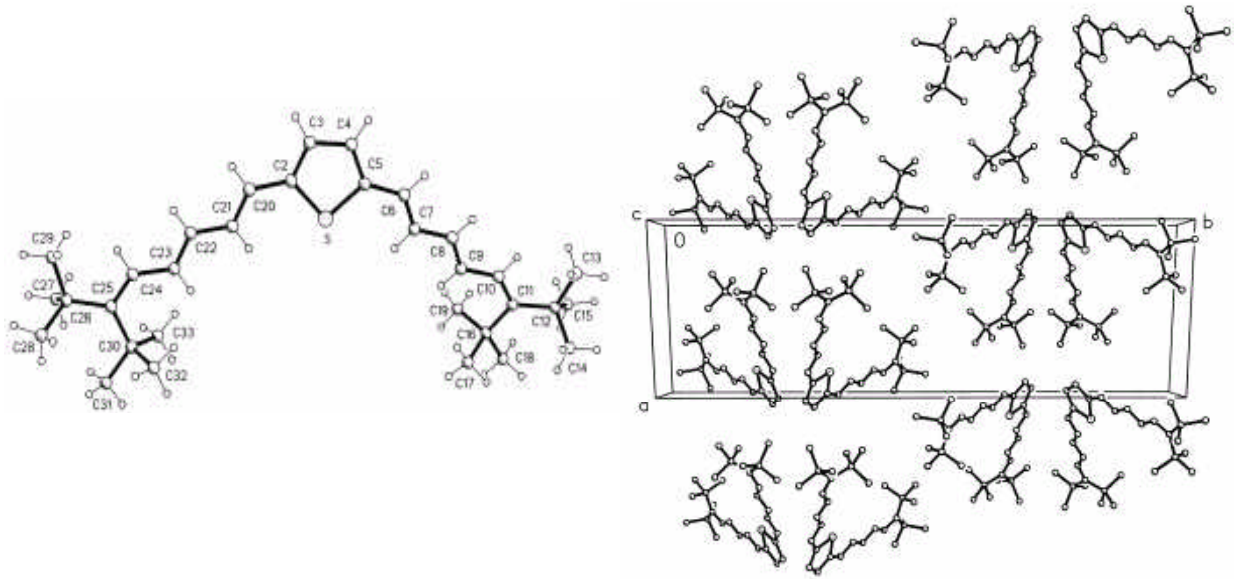


The thiophenes **230** and **231** are highly stable compounds and no decomposition was observed even upon melting. Their recrystallization from ethanol gave crystals suitable for X-ray structure analyses (Fig. 22, 23).



Unit cell dimensions: a = 2275.79 (16) pm, b = 2275.79 (16) pm, c = 1965.08 (18) pm; $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$.

Figure 22. Structure of **230** in the crystal and its crystal packing diagram.



Unit cell dimensions: a = 1164.8 (5) pm, b = 3391.7 (6) pm, c = 820.2 (4) pm; $\alpha = 90°$, $\beta = 109.08$ (4)°, $\gamma = 90°$.

Figure 23. Structure of **231** in the crystal and its crystal packing diagram.

Both thiophenes **230** and **231** are fluorescent and their absorption and fluorescent emission-excitation spectra were studied in dichloromethane. The fluorescence spectra were measured by excitation of the samples at 380 nm. While the absorption spectrum of compound **230** shows no significant vibrational structure (Fig. 24), the bands of the absorption spectrum of **231** are resolved and show vibrational fine structure (Fig. 25). The bands in the fluorescence spectra of both compounds are very broad (Fig. 26 and 27). There is no mirror image relation ship between the excitation and emission spectra of the compounds. Deviations from the mirror image rule usually indicates a geometric rearrangement of the molecules in the excited state as compared to the ground state. Other than geometric rearrangements, excited-state reactions or complex formation of the fluorophores with each other can also cause deviations from the mirror image rule.[81]

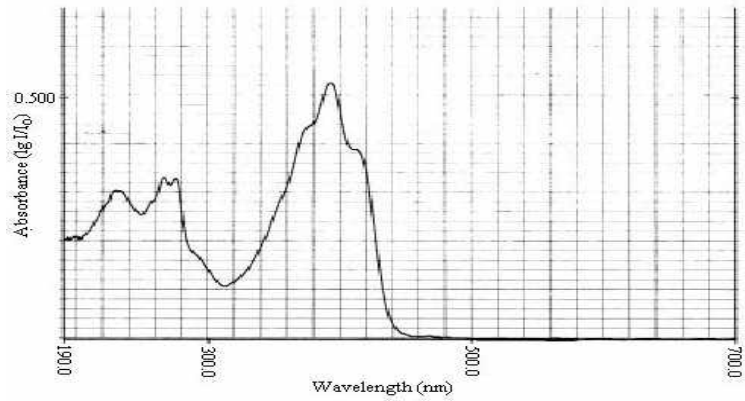


Figure 24. UV/Vis absorption spectrum of **230** in dichloromethane.

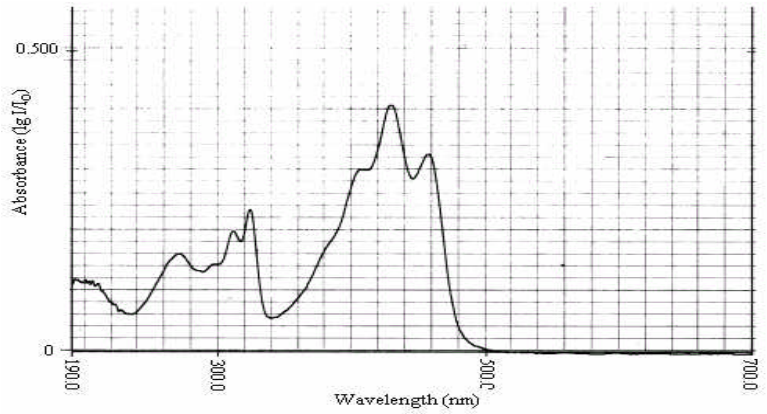


Figure 25. UV/Vis absorption spectrum of **231** in dichloromethane.

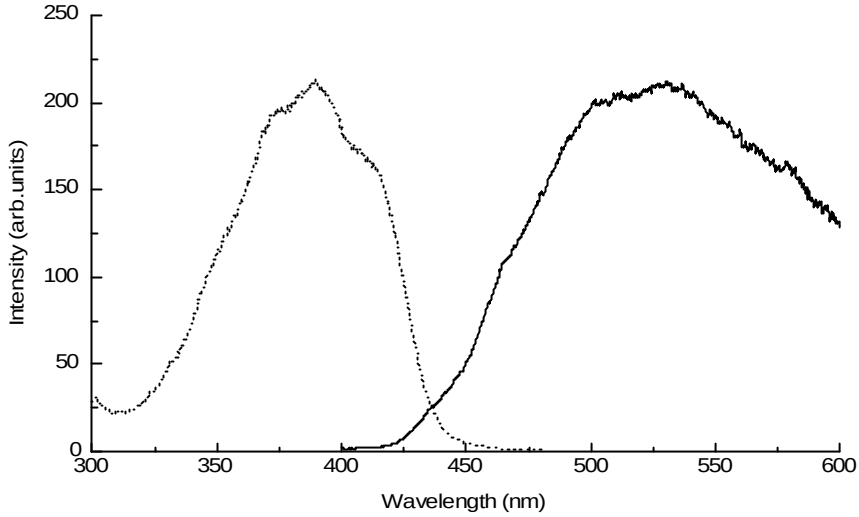


Figure 26. Fluorescent emission-excitation spectrum of **230** (.....excitation spectrum , - emission spectrum) in dichloromethane.

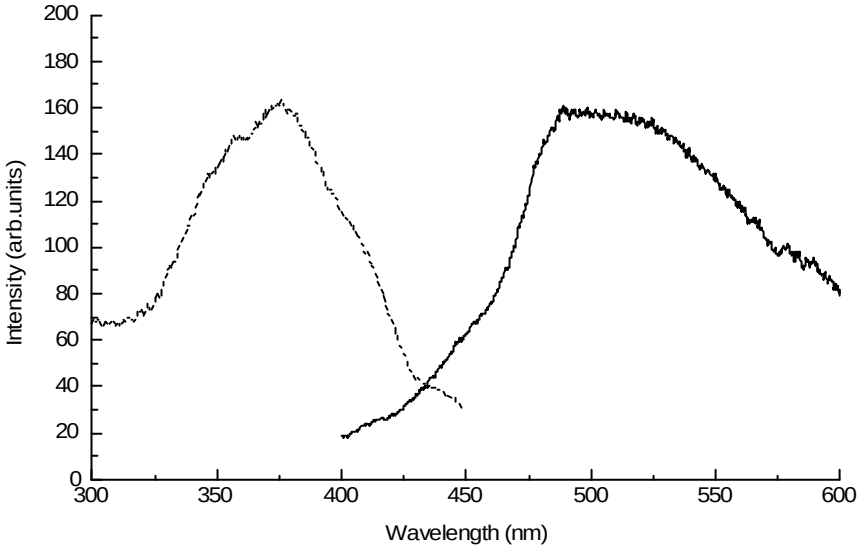
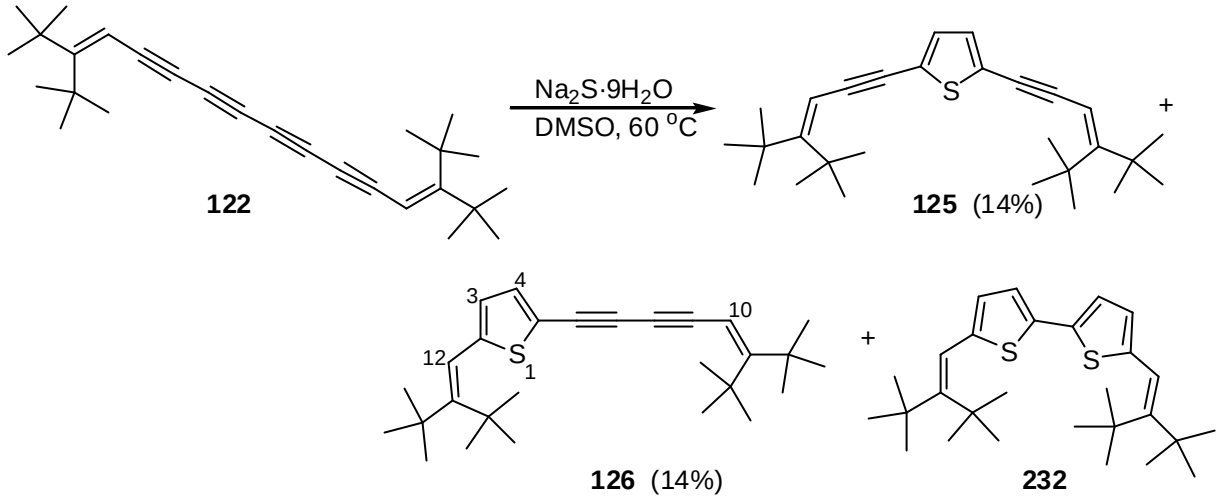


Figure 27. Fluorescent emission-excitation spectrum of **231** (.....excitation spectrum , - emission spectrum) in dichloromethane.

The tetraacetylene **122** was also treated with $Na_2S{\cdot}9H_2O$ in DMSO and the products obtained were purified and separated by chromatography on silica gel with ethylacetate/hexane (1:10). Both compounds **125** and **126** were formed in ca. 14% yield (Exp. 4.3.67). The third product, detected by TLC, could not be characterized fully because of its very low amount (~ 5mg). However, from its mass spectrometric analysis,

which showed the existence of a second sulfur atom and 2 more hydrogen atoms, the compound very likely is **232.**



The hydrocarbon **125** absorbs over a very broad range and the spectrum does not show any vibrational fine structure; the band intensities are quite low (Fig. 28). The absorption spectrum of compound **126** also shows a broad band; however, the band intensity was much higher in comparison with that of **125** (Fig. 29). Both thiophenes are orange coloured solids.

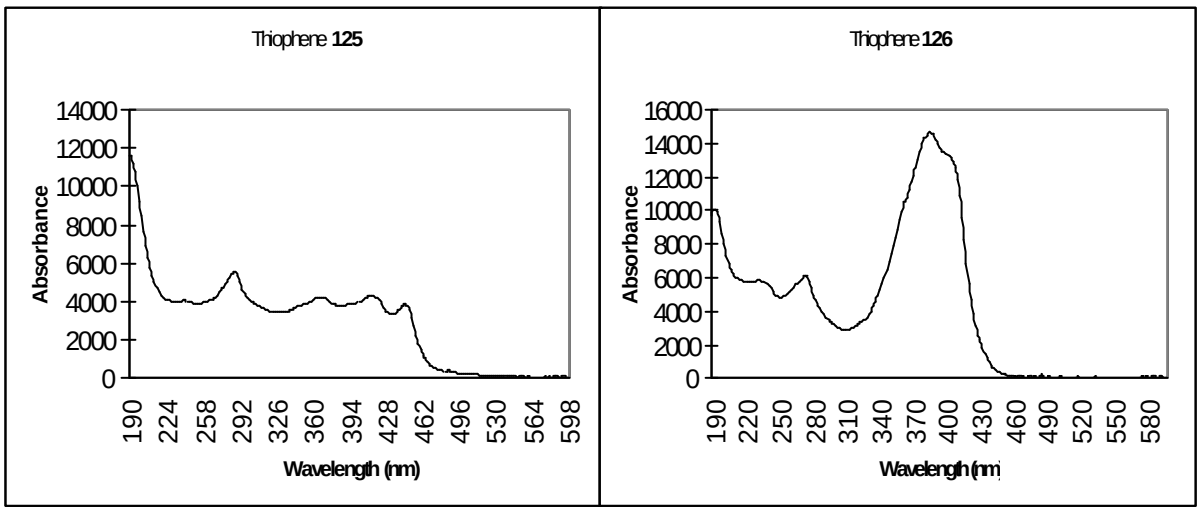


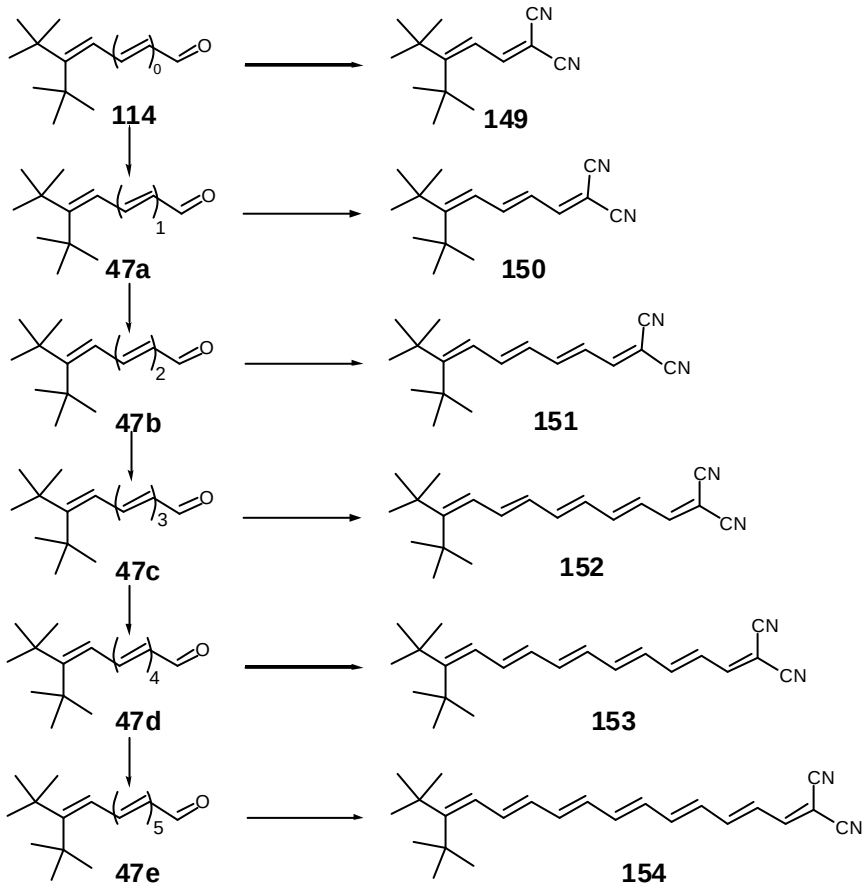
Figure 28. UV/Vis absorption spectrum of **125** in acetonitrile.

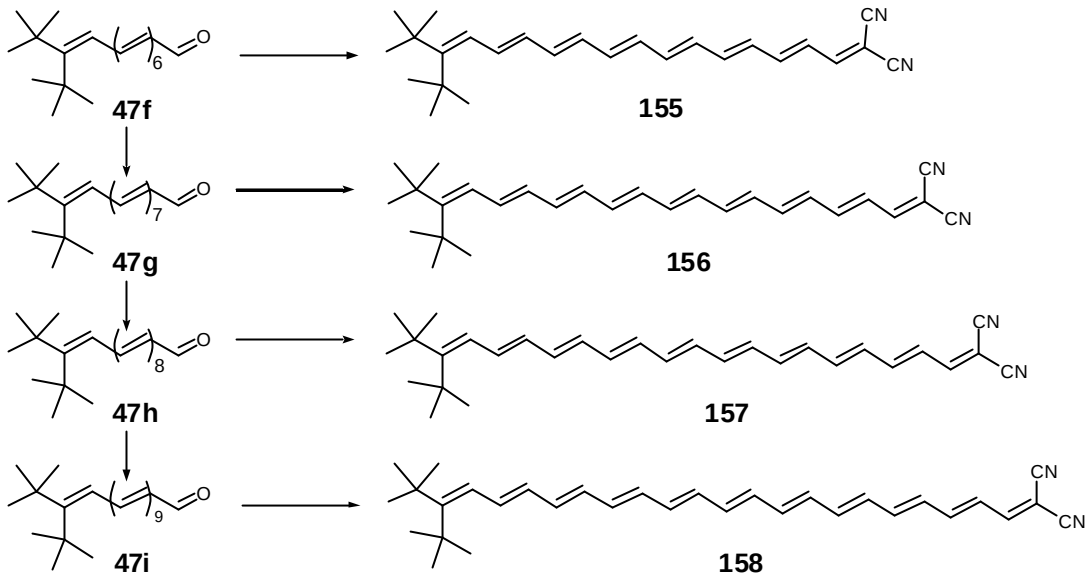
Figure 29. UV/Vis absorption spectrum of **126** in acetonitrile.

3. Summary

The aim of this study was to prepare a series of sterically protected polyenes and polyenynes and to investigate their structural, spectroscopic and chemical properties. The bulky *tert*-butyl groups are necessary for protection/ stabilization of the prepared and studied systems.

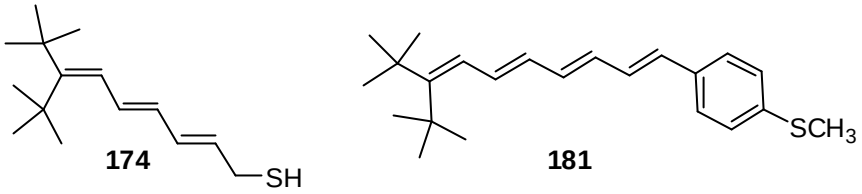
3.1 In the first part of this investigation the synthesis of dicyano group functionalized polyenes is described. Towards this end a series of polyene aldehydes 47a-h was synthesized first, of which the series up to 6 double bonds had already been prepared earlier.[23] The conjugation of the systems was extended up to 10 double bonds. Then, by Knoevenagel condensation of these aldehydes with malononitrile, the all-*trans* α-dicyano polyenes, 159-168, with up to 11 double bonds were prepared.



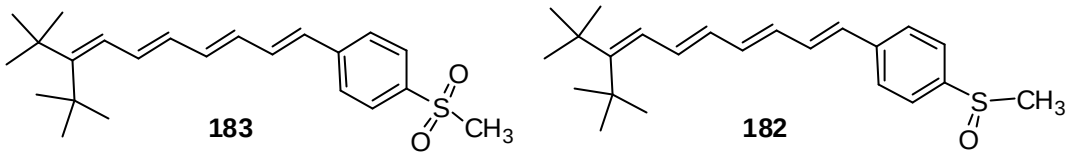


The polyene aldehydes up to 8 double bonds are highly soluble in polar organic solvents and stable. However, from 8 double bonds on first the solubility, and, then, from 9 double bonds on, the stability of the aldehydes decreases dramatically. On the other hand the dicyano functionalized compounds are stable and soluble even when there are 11 conjugated double bonds. The novel polyenes were characterized by conventional techniques (NMR, MS and IR spectroscopy, X-ray crystallography), as well as by a detailed UV/Vis analysis. As expected, the increase in chain length causes absorption at higher wavelengths. The introduction of the electron withdrawing cyano groups causes intense absorption bands in the visible region. No significant solvent effect (solvatochromism) was found for compounds 162 and 164 in solvents of different polarity.

3.2 In the second part of this disertation polyenes with different sulfur derived functional groups were prepared. It was found that the conjugated polyenes with a thiol end group (**174**) were highly unstable despite di-*tert*-butyl protection at the ω-position. However, stable derivatives like thioether **181**, sulfoxide **182**, or sulfone **183** could be prepared. It is a challenging goal to attach the synthesized derivatives to metal surfaces like gold or silver and prepare monolayers.[49-51]

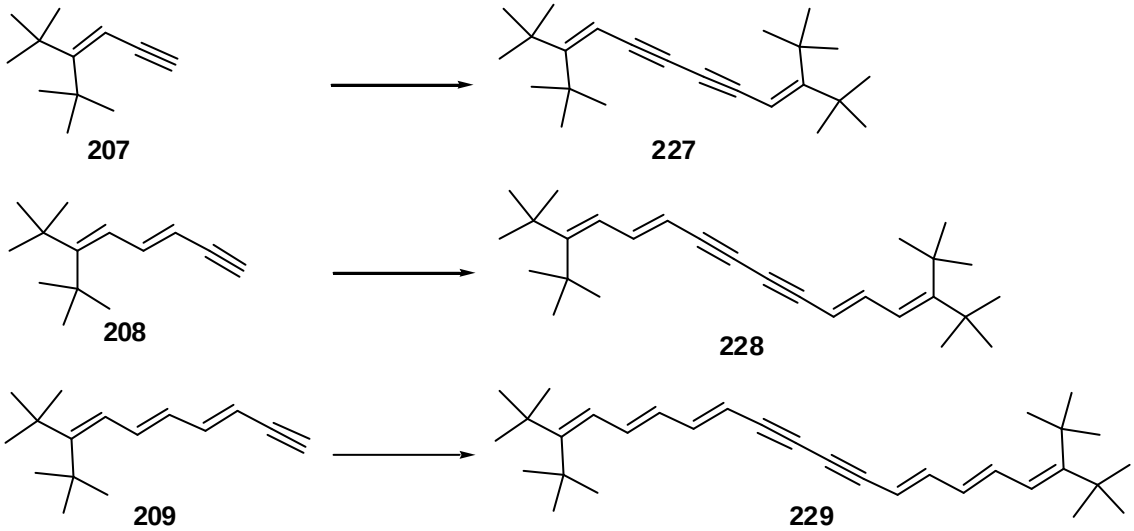


174 **181**



183 **182**

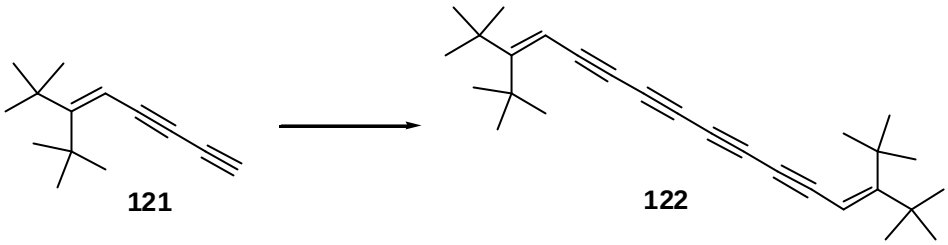
3.3 In the third part tetra-*tert*-butyl protected polyenediyne and polyenetetraeyne systems were prepared. Towards this end all necessary terminal acetylenes, **207**, **208**, **209**, **121**, were prepared first, which were then, by oxidative coupling reactions, converted to the diacetylenes **227**, **228**, **229**, and tetraacetylene **122**. All compounds were stable and their X-ray analyses could be performed. For an all-carbon tetraacetylene system this constituets the first reported example. The packing diagrams of all hydrocarbons show that the bulky *tert*-butyl groups prevent the molecules to come too close to each other, one of the reson for the stability of the compounds.



207 **227**

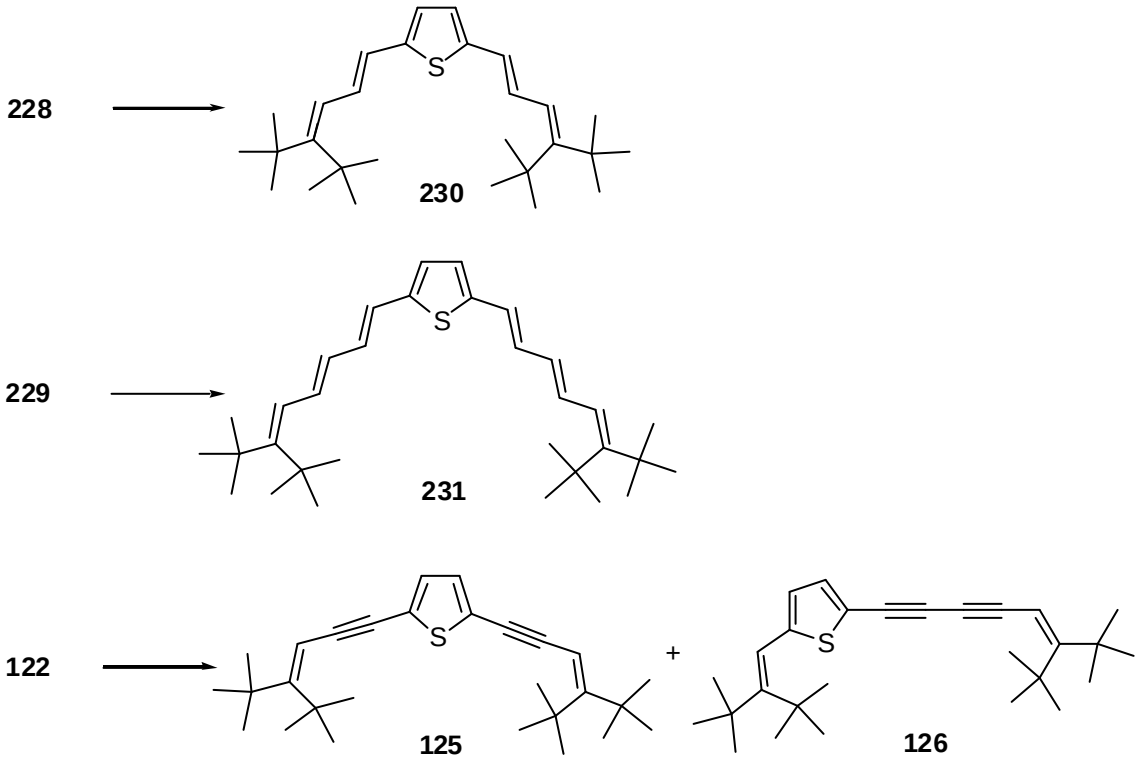
208 **228**

209 **229**



3.4 In the last part of the present work the reactivities of di- and tetraacetylene systems **227**, **228**, **229**, **122** towards the formation of thiophene derivatives with $Na_2S{\cdot}9H_2O$ were studied. The smallest diacetylene **227** was found out to be inert towards the formation of a thiophene derivative, suggesting that steric hindrance caused by the bulky *tert*-butyl groups prevents the addition process. Diacetylenes **228** and **229** gave the desired thiophenes **230** and **231** readily in excellent yields. The compounds were fluorescent and their fluorescence properties have been investigated. The stable thiophenes **230** and **231** are of potential use as components in molecular electronics.

From the reaction of the tetraacetylene **122** with $Na_2S{\cdot}9H_2O$ two products resulted: **125**, **126**.



4. Experimental

4.1 Instrumentation and general experimental considerations

Thin Layer Chromatography (TLC):

Silica gel (SiO_2): " Polygram Sil G/UV_{254}" , Macherey-Nagel & Co. (Düren).

Column Chromatography:

Silica gel (SiO_2): Silica gel 60 (70-230 mesh), Merck (Darmstadt).

Melting Points:

Measurements below 200 °C were made on a Büchi 510 melting point apparatus and above 200 °C were made on a Kofler-Heiztischmikroskop apparatus. The melting points are uncorrected.

Sublimation:

A temperature gradient sublimer from Esoteric Chemicals was used.

NMR Spectroscopy:

^1H and ^{13}C NMR spectra were recorded on the following spectrometers;

Bruker AC-200 ^1H NMR (200.1 MHz); ^{13}C NMR (50.3 MHz);

Bruker AM-400 ^1H NMR (400.1 MHz); ^{13}C NMR (100.6 MHz);

Bruker DRX-400 ^1H NMR (400.1 MHz); ^{13}C NMR (100.6 MHz).

Deuteriochloroform ($CDCl_3$) was used as the NMR solvent. Chemical shifts are reported in parts per million (d) downfield from the internal tetramethylsilane reference. Spin multiplicities are indicated by the following symbols; s (singlet), d (doublet), t (triplet), m (multiplet).

IR Spectroscopy:

IR spectra were recorded on a Nicolet 320 FT-IR spectrometer. Samples were prepared either as KBr pellets or as thin films. Band postions are reported in reciprocal centimeters. Band intensities are referred by the following symbols; vs (very strong), s (strong), m (medium), w (weak).

UV/Vis Spectroscopy:

UV spectra were recorded on a HP 8452 A Diode Array Spectrophotometer.

Fluorescence Spectroscopy:

Fluorescence emission-excitation spectra were recorded on a HITACHI F4500 model fluorescence spectrometer (Department of Chemistry, IIT-Madras, India) and the emission spectra were corrected for the instrument response.

Mass Spectrometry:

Mass spectra were recorded on a Finnigan MAT 8430 spectrometer using either electron ionization (EI, 70 eV) or fast-atom bombardment (FAB) method.

GC/MS:

GC/MS spectra were recorded on a Finnigan MAT 4515 (EI, 40eV) mass spectrometer attached to a Carlo Erba HRGC 5160 gas chromatograph.

Elemental Analysis:

Analyses were carried out at the Institut für Pharmazeutische Chemie, TU Braunschweig.

X-ray analysis:

The following diffractometers were used for the X-ray structure analyses;

Siemens R3; Stoe STADI-4; Bruker SMART 1000 CCD

The X-ray data were processed and refined with the SHELXS-86 and SHELXS-93 programs.

4.2 General experimental procedures

General procedure 1:

To a stirred suspension of 2.5 equivalents of phosphonium salt **141** in anhydrous THF was added 2.4 equivalents of *t*-BuOK under N_2. An immediate colour change from white to yellow was observed. After 30 min stirring 1 equivalent of the respective aldehyde in THF was added dropwise and stirring continued for 6 h. Seven equivalents of aqueous oxalic acid solution was added and the reaction was left overnight stirring. After the phases were separated the aqueous phase was extracted several times with Et_2O. The combined organic phases were neutralized with saturated $NaHCO_3$ solution, dried with anhydrous $MgSO_4$, and the solvent was removed in a rotary evaporator. The remaining residue was purified by column chromatography on silica gel.

General procedure 2:

To anhydrous THF cooled to −78 °C first 1.1 equivalent of diisopropylamine then 1.1 equivalent of *n*-BuLi (1.6 M in hexane) were added under N_2. After 10 min stirring 1.1 equivalent of phosphonocrotonate **147** in THF was added dropwise and the reaction was stirred for 30 additional min. Then was added 1 equivalent of the aldehyde and the reaction left to warm to room temp. The reaction mixture was hydrolyzed and the phases were separated. The aqueous phase was extracted several times with Et_2O. The combined organic phases were dried with anhydrous $MgSO_4$. After solvent evaporation the remaining residue was purified by column chromatography on silica gel.

General procedure 3:

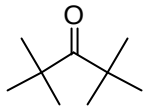
2.5 equivalents of DIBAL (1.5 M in hexane) was added dropwise to a solution of 1 equivalent of ester in anhydrous toluene at −78 °C. With the first drops of DIBAL the light colour of the solution got darker and when all the ester had been reduced the colour changed to light again. After stirring for 10 min at the same temperature 3 equivalents of

50% aqueous acetic acid solution was added and the cooling was removed. Formation of a colourless gel was observed. The mixture was filtered through celite and washed with acetone. After solvent removal in vacuo the crude product was used without further purification.

General procedure 4:

A mixture of 1 equivalent of aldehyde, 1 equivalent of malononitrile and 0.01 equivalent of β-alanine was stirred for 1.5 h in refluxing 95% EtOH under N_2. When the reaction was cooled to room temp. crystal formation was observed. The precipitate was dissolved with Et_2O and the solution was diluted with water. After the separation of phases the aqueous phase was extracted several times with Et_2O. The combined organic phases were dried with anhydrous $MgSO_4$, the solvent was evaporated, and the residue was purified by recrystallization from hexane.

4.3.1: 2,2,4,4-tetramethyl-3-pentanone (126)

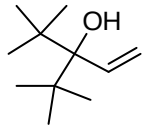


126

To a mixture of 36 g (1.5 mol) Mg in anhydrous THF (150 mL) was added about 30 mL of a solution of 138.9 g (1.5 mol, 163.2 mL) *tert*-butylchloride in THF (300 mL) and a few drops of 1,2-dibromoethane under N_2. When the exothermic reaction started the reaction mixture was cooled to 35 °C and the rest of the *tert*-butylchloride solution was added dropwise in about 3.5 h. The reaction mixture was stirred for an additional 30 min and when all Mg turnings had dissolved it was transferred to a dropping funnel under N_2. A mixture of 5.5 g (0.087 mol) Cu, 25.1 g (0.255 mol) CuCl and 58.2g (0.48 mol, 60 mL) pivaloyl chloride (**125)** in anhydrous THF (250 mL) was cooled to –40 - –45 °C and the above Grignard reagent was added to this solution very slowly. Through out the addition process the reaction temperature was kept beween –40 and –45 °C (about 3.5 h). When the addition was complete the mixture was stirred for an other 45 min at –40 °C and then left to warm up to room temp. slowly. After 30 min stirring at room temp. it was carefully hydrolyzed with ice-water. The formed black precipitate was dissolved with saturated NH_4Cl solution and the mixture was extracted several times with Et_2O. The combined organic phases were dried with $MgSO_4$, filtered and the solvent was removed in a rotary evaporator. 54.5 g (0.38 mol, 80%: ref. 68% [23b]) of pure ketone **126** was obtained after vacuum distillation at 80 °C / 75mbar.

The spectral data of **126** agree with the data given in ref.[23b]

4.3.2: 3-(*tert*-Butyl)-4,4-dimethyl-1-penten-3-ol (128)

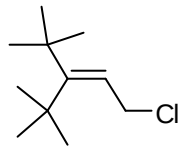


128

To a suspension of 47.4 g (1.95 mol) Mg in anhydrous THF (210 mL) was added a 50 mL solution of 110 mL (164.5 g, 1.54 mol) of vinylbromide in anhydrous THF (610 mL) and a few drops of 1,2-dibromoethane under N_2. After the exothermic reaction started the mixture was cooled to 35 °C and the rest of the vinylbromide solution was added dropwise in ca. 2 h. When the addition was complete the reaction mixture was stirred for an additional 30 min and after all the Mg turnings had dissolved it was cooled to 0 °C. To this solution was added 46 g (0.324 mol) of **126** dropwise in 2 h. When the addition was over the reaction was left to warm to room temp. slowly and stirring was continued for 2 more h. The mixture was hydrolyzed carefully with ice-water, and the formed white precipitate was dissolved with saturated NH_4Cl solution. After separation of the phases the aqueous phase was extracted several times with Et_2O. The combined organic phases were dried with $MgSO_4$, filtered and the solvent was removed. Distillation at 100 °C/ 40 mbar yielded 47.6 g (0.28 mol, 85%: ref.: 90%[23b]) alcohol **128** as a colourless liquid.

The spectral data of **128** agree with the data given in ref.[23b]

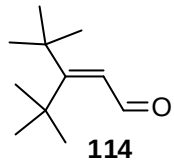
4.3.3: 1-Chloro-3-(*tert*-butyl)-4,4-dimethyl-2-pentene (129)



To a cooled solution (0 °C) of 34.10 g (0.2 mol) of **128** and 19.26 g (0.24 mol, 19.7 mL) of pyridine in anhydrous Et_2O (110 mL) was added dropwise a solution of 58 g (0.49 mol, 36 mL) $SOCl_2$ in anhydrous Et_2O (70 mL) under N_2 during 1h. When the addition was complete the reaction was left to warm to room temp. and stirred for another 2 h. Decomposition with ice-water, separation of the phases, and extraction of the aqueous phase several times with Et_2O followed. The combined organic phases were dried with $MgSO_4$, and the solvent was removed in a rotary evaporator. Distillation at 60 °C/ 0.7 mbar gave the chloride **129** in 60 % yield (22.62 g, 0.12 mol) as a colourless liquid.

The spectral data of the compound **129** agree with the data given in ref.[23b]

4.3.4: 3-(*tert*-Butyl)-4,4-dimethyl-2-pentenal (114)



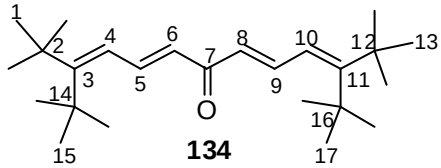
114

To a solution of 4.48 g (80 mmol) KOH in H_2O (16 mL) and 2-propanol (58 mL) was slowly added 10.1 mL (0.11 mol) of freshly distilled 2-nitropropane under N_2. After 30 min 11.0 g (0.58 mmol mol) of **129** in 2-propanol (58 mL) was added dropwise and the reaction mixture was refluxed for 5.5 h. During reflux a light yellow precipate formed. The mixture was cooled to room temp., diluted with H_2O and extracted several times with Et_2O. The combined organic phases were dried with $MgSO_4$, the solvent was evaporated and the residue was purified by column chromatography on silica gel with ethyl acetate/ hexane = 1:7 (v/v) to give 7.90 g (47 mmol, 80%: ref.: 66%[23b]) **114** as a colorless liquid. In this reaction 0.6 g (5 %) of **131** as a light yellow oil and 0.15 g (0.7%) of **132** as a greenish yellow solid were formed as side products.

B.p. 84 °C/ 1 mbar (Lit.[23b] 65 °C/ 0.5 mbar).
R_F (EtOAc/hexane = 1:7): 0.50.

The spectral data of **114** agree with the data given in ref.[23b]

4.3.5: 3,11-Di-*tert*-butyl-2,2,12,12-tetramethyl-trideca-3,5,8,10-tetraen-7-one (134)



134

One half of a mixture of 0.2 g (1.19 mmol) **114** and 44 mL (5.95 mmol) of acetone was added to a stirred solution of 0.12 g (3 mmol) NaOH in H_2O (1.2 mL) and ethanol (1 mL). The clear colourless solution turned to pale yellow and turbid. After 15 min the other half of the aldehyde-acetone mixture was added causing the colour to turn to bright

yellow. The mixture was stirred overnight, diluted with water and extracted with Et_2O. The organic phase was dried with $MgSO_4$. After solvent evaporation the residue was purified on silica gel using ethylacetate/ hexane = 3:10 (v/v) yielding 0.15 g (4.19 mmol, 69 %) **134** as a bright yellow oil. Besides 53 mg (2.5 mmol, 23 %) of **131** was formed.

3,11-Di-*tert*-butyl-2,2,12,12-tetramethyl-trideca-3,5,8,10-tetraen-7-one (134)

R_F (EtOAc/hexane = 3:10): 0.47.

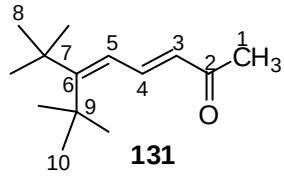
^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.26 , 1.42 (s, 36 H, 1/13/15/17-H), 6.20 (d, 2 H, $^3J_{4\text{-H, }5\text{-H}}$ = 11.8 Hz, 4/10-H), 6.25 (d, 2 H, $^3J_{6\text{-H, }5\text{-H}}$ = 14.7 Hz, 6/8-H), 8.01 (dd, 2 H, $^3J_{5\text{-H, }6\text{-H}}$ = 14.7 Hz and $^3J_{5\text{-H, }4\text{-H}}$ = 11.9 Hz, 5/9-H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 189.52 (s, C-7), 168.07 (s, C-3/11), 141.60 (d, C-6/8), 128.33 (d, C-5/9), 122.60 (d, C-4/10), 39.63, 38.60 (s, C-2/12/14/16), 34.30, 31.47 (q, C-1/13/15/17).

IR (KBr): $\tilde{n}$ = 2957 cm^{-1} (s), 1663 (C=O, m), 1600 (C=C, s), 1483 (w), 1366 (w), 1289 (w), 1212 (w).

MS (70 eV): *m*/*z* (%) =358 [M^+] (5), 302 (57), 245 (37), 218 (15), 175 (13), 152 (13), 137 (40), 109 (78), 57 [*t*-Bu] (100).

6-*tert*-Butyl-7,7-dimethyl-octa-3,5-dien-2-one (131)



131

R_F (EtOAc/hexane = 3:10): 0.30.

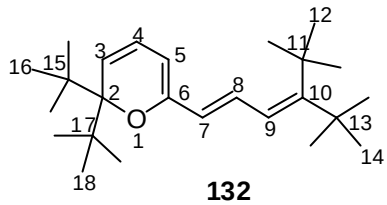
^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.25, 1.42 (s, 18 H, 8/10-H), 2.28 (s, 3 H, 1-H), 6.01 (d, 1 H, $^3J_{3\text{-H, }4\text{-H}}$ = 15.0 Hz, 3-H), 6.14 (d, 1 H, $^3J_{5\text{-H, }4\text{-H}}$ = 11.7 Hz, 5-H), 7.87 (dd, 1 H, $^3J_{4\text{-H, }3\text{-H}}$ = 15.1 and $^3J_{4\text{-H, }5\text{-H}}$ = 11.7 Hz, 4-H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 198.46 (s, C-2), 168.10 (s, C-6), 142.21 (d, C-3), 129.45 (d, C-4), 122.18 (d, C-5), 39.61, 38.51 (s, C-7/9), 34.23, 31.41 (q, C-8/10), 25.55 (q, C-1).

IR (KBr): $\tilde{n}$ = 2959 cm^{-1} (s), 1687 (C=O, m), 1665s (C=C, m), 1608 (m), 1594 (s), 1367 (m), 1251 (m), 1214 (m).

MS (70 eV): *m*/*z* (%) = 208 [M^+] (2), 192 (5), 191 (8), 153 (12), 152 (80), 151 (20), 137 (34), 109 (94), 57 [*t*-Bu] (100), 43 (78).

4.3.6: 2,2-Di-*tert*-butyl-6-(4-*tert*-butyl-5,5-dimethyl-hexa-1,3-dienyl)-2H-pyran (132)



132

A solution of 90 mg (0.25 mmol) of ketone **134** in 2-propanol (7 mL) was added to an aqueous solution of KOH (1M, 5mL) and the mixture was refluxed for 8 h. After cooling to room temp. it was diluted with water and extracted several times with Et_2O. The combined organic phases were dried with $MgSO_4$, and after removal of the solvent, the residue was purified on silica gel using ethylacetate/hexane = 3:10 (v/v) as the eluent: 12 mg (0.004 mmol, 14%) of **132** as a greenish yellow solid, m.p. 128-130 °C.

In another experiment a mixture of 15 mg (0.04 mmol) ketone **134** and a small crystal of *p*-toluene sulfonic acid in C_6D_6 (0.6 mL) was heated at 60 °C and the reaction was monitored by ^{1}H NMR spectroscopy. After 16 h the 2H-pyran **132** and the ketone **134** were determined to be present in a 1: 3.4 ratio of according to the peak integration in the ^{1}H NMR spectrum.

R_F (EtOAc/hexane = 3:10): 0.92.

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.08 (s ,18 H, 16/18-H), 1.23, 1.41 (s, 18 H, 12/14-H), 4.89 (d, 1 H, $^3J_{3\text{-H, }4\text{-H}}$ = 6.0 Hz, 3-H), 5.42 (d, 1 H, $^3J_{5\text{-H, }4\text{-H}}$ = 10.4 Hz, 5-H), 5.70 (d, 1 H, $^3J_{7\text{-H, }8\text{-H}}$ = 14.6 Hz, 7-H), 5.91 (dd, 1 H, $^3J_{4\text{-H, }3\text{-H}}$ = 6.0 and $^3J_{4\text{-H, }5\text{-H}}$ = 10.4 Hz, 4-H),

6.11 (d, 1 H, $^{3}J_{9\text{-H, }8\text{-H}}$ = 12.0 Hz, 9-H), 7.35 (dd, 1 H, $^{3}J_{8\text{-H, }9\text{-H}}$ = 12.0 Hz and $^{3}J_{8\text{-H, }7\text{-H}}$ = 14.6 Hz, 8-H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 158.3 1 (s, C-10), 152.40 (s, C-2), 128.09, 125.02, 123.19, 120.76, 119.73 (d, C-4/5/7/8/9), 98.48 (d, C-3), 89.02 (s, C-6), 43.50 (s, C-15/17), 38.93, 37.92 (s, C-11/13), 33.63, 31.77 (q, C-12/14), 25.55 (q, C-16/18).

IR (KBr): $\tilde{n}$ = 2958 cm^{-1} (s), 1642 (C-O, m), 1542m (C=C, m), 1481 (m), 1388 (m), 1365 (m), 1332 (m), 1060 (s), 1007 (m), 716 (m).

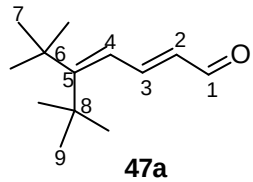
MS (70 eV): *m*/*z* (%) =358 [M^+] (2), 302 (24), 301 (100), 245 (32), 244 (34), 230 (4), 229 (20), 222 (18), 57 [*t*-Bu] (20).

UV ($CHCl_3$): λ_{max} (lg ε) = 310 nm (3.89), 330 (4.08), 350 (4.23), 365 (4.22), 405 (3.56).

HRMS: $C_{25}H_{42}O$ (358.6), Calc. 358.3235

Found 358.3224 ± 2 ppm

4.3.7: 5-(*tert*-butyl)-6,6-dimethyl-2,4-heptadienal (47a)



47a

General procedure 1

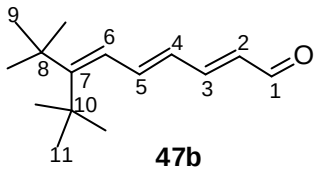
3g (0.018 mol) **114** in 30 mL of THF; 19.15 g (0.044 mol) **141** in 90 mL of THF; 4.81 g (0.043 mol) *t*-BuOK; 15.76 g (0.125 mol) oxalic acid in 125 mL of water.

Product was purified by column chromatography on silica gel with ethylacetate/hexane = 1:10 (v/v): 3.00 g (0.0155 mol, 86%; lit. 70%[23b]), low melting (~ 5°C) colourless solid.

R_F (EtOAc/hexane = 1:10): 0.55.

The spectral data of **47a** agree with the data given in ref.[23b]

4.3.8: 7-(*tert*-Butyl)-8,8-dimethyl-2,4,6-nonatrienal (47b)



47b

General procedure 1

2.46 g (12.7 mmol) **47a** in 25 mL of THF; 13.65 g (31.8 mmol) **141** in 60 mL of THF; 3.42 g (30.5 mmol) *t*-BuOK; 11.34 g (90.0 mmol) oxalic acid in 90 mL of water.

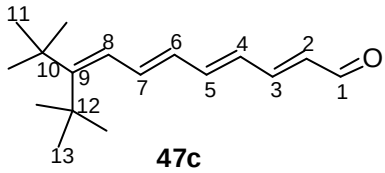
Product was purified by column chromatography on silica gel with ethylacetate/hexane = 1:10 (v/v): 2.45 g (11.1 mol, 88%; lit. 78%[23b]), yellow solid.

R_F (EtOAc/hexane = 1:10): 0.61.

M.p. 30-31 °C.

The spectral data of **47b** agree with the data given in ref. [23b]

4.3.9: 9-(*tert*-Butyl)-10,10-dimethyl-2,4,6,8-undecatetraenal (47c)



47c

General procedure 1

1.15 g (5.23 mmol) **47b** in 10 mL of THF; 5.60 g (13.0 mmol) **141** in 25 mL of THF; 1.40 g (12.5 mmol) *t*-BuOK; 4.61 g (36.0 mmol) oxalic acid in 36 mL of water.

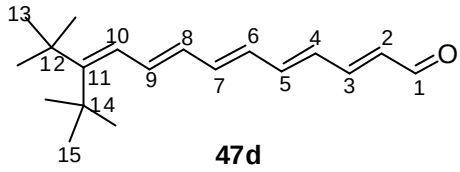
Product was purified by column chromatography on silica gel with ethylacetate/hexane = 1:10 (v/v): 1.168 g (4.74 mmol, 91%; lit. 87%[23b]), yellow solid.

R_F (EtOAc/hexane = 1:10): 0.51.

M.p. 43-45 °C.

The spectral data of **47c** agree with the data given in ref.[23b]

4.3.10: 11-(*tert*-Butyl)-12,12-dimethyl-2,4,6,8,10-tridecapentaenal (47d)



47d

General procedure 1

0.70 g (2.85 mmol) **47c** in 5 mL of THF; 3.05 g (7.11 mmol) **141** in 15 mL of THF; 0.77 g (6.83 mmol) *t*-BuOK; 2.52 g (20.0 mmol) oxalic acid in 20 mL of water.

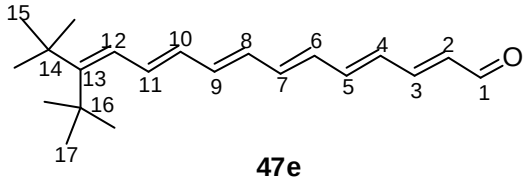
Product was purified by column chromatography on silica gel with ether/petrolether = 3:10 (v/v): 0.75 g (2.76 mmol, 96%; lit. 92%[23b]), yellow solid.

R_F (Ether/petrolether = 3:10): 0.61.

M.p. 84-85 °C.

The spectral data of **47d** agree with the data given in ref.[23b]

4.3.11: 13-(*tert*-Butyl)-14,14-dimethyl-2,4,6,8,10,12-pentadecahexaenal (47e)



47e

General procedure 1

0.53 g (1.95 mmol) **47d** in 4 mL of THF; 2.10g (4.87 mmol) **141** in 10 mL of THF; 0.52 g (4.67 mmol) *t*-BuOK; 1.72 g (13.6 mmol) oxalic acid in 13.6 mL of water.

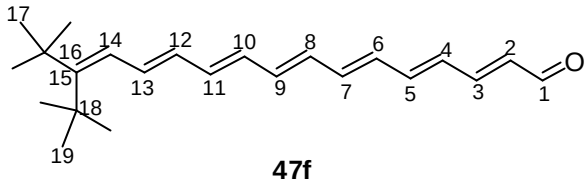
Product was purified by column chromatography on silica gel with ethylacetate/hexane = 1: 6 (v/v): 0.54 g (1.81 mmol, 93%; lit. 93%[23b]), orange solid.

R_F (EtOAc/hexane = 1:6): 0.58.

M.p. 127 °C.

The spectral data of **47e** agree with the data given in ref.[23b]

4.3.12: 15-(*tert*-Butyl)-16,16-dimethyl-2,4,6,8,10,12,14-heptadecaheptaenal (47f)



47f

General procedure 1.

0.29 g (0.97 mmol) **47e** in 7 mL of THF; 1.04 g (2.43mmol) **141** in 15 mL of THF; 0.262 g (2.34 mmol) *t*-BuOK; 0.86 g (6.81 mmol) oxalic acid in 6.80 mL of water.

Product was purified by column chromatography on silica gel with CH_2Cl_2: 0.30g (0.93 mmol, 95%), red solid.

R_F (CH_2Cl_2): 0.63.

M.p. 140-141 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.23, 1.37 (s, 18 H, H-17/19), 6.08 (d, 1 H, $^3J_{14\text{-H},\ 13\text{-H}}$ = 11.7 Hz, 14-H), 6.12-6.19 (m, 2 H, 14/2-H), 6.25-6.37 (m, 2 H, 10/8-H), 6.41-6.57 (m, 3 H, H-4/6/7), 6.72 (dd, 1 H, $^3J_{5\text{-H},\ 4\text{-H}}$ = 14.7 Hz and $^3J_{5\text{-H},\ 6\text{-H}}$ = 11.3 Hz, 5-H), 6.91 (dd, 1 H, $^3J_{13\text{-H},\ 12\text{-H}}$ = 14.1 Hz and $^3J_{13\text{-H},\ 14\text{-H}}$ = 12.0 Hz, 13-H), 7.14 (dd, 1 H, $^3J_{3\text{-H},\ 2\text{-H}}$ = 15.0 Hz and $^3J_{3\text{-H},\ 4\text{-H}}$ = 11.3 Hz, 3-H), 9.56 (d, 1 H, $^3J_{1\text{-H},\ 2\text{-H}}$ = 7.9 Hz, 1-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 193.38 (d, C-1), 159.24 (s, C-15), 151.81 (d, C-3), 142.80 (d, C-5), 139.11, 137.00, 136.20, 134.37, 132.04, 131.77, 131.68, 131.20, 130.62, 129.54 (d, C-2/4/6/7/8/9/10/11/12/13), 123.94 (d, C-14), 39.07, 38.01 (s, C-16/18), 33.77, 31.70 (q, C-17/19).

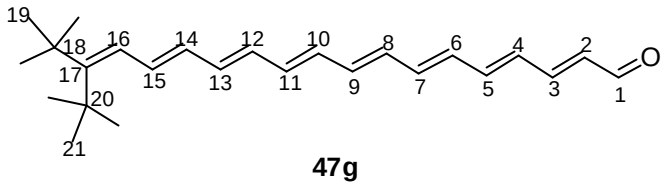
IR (KBr): $\tilde{n}$ = 1957 cm^{-1} (m), 1667 (C=O, s), 1613 (m), 1542 (C=C, s), 1482 (w), 1392 (w), 1216 (w), 1114 (s), 1105 (s), 1007 (vs).

MS (70 eV): *m*/*z* (%) = 324 [M^+] (100), 289 (35), 267 (88), 262 (10), 240 (20), 197 (12), 162 (100), 147 (42), 131 (58), 105 (44), 91 (100), 77 (66), 72 (66), 72 (79), 57 [M^+-*t*-Bu].

UV ($CHCl_3$): λ_{max} (lg ε) = 422 nm (4.80).

Although all the spectroscopic data are consistent with the proposed structure, elemental analysis of this substance did not yield satisfactory elemental composition.

4.3.13: 17-(*tert*-Butyl)-18,18-dimethyl-2,4,6,8,10,12,14,16-nonadecaoctaenal (47g)



47g

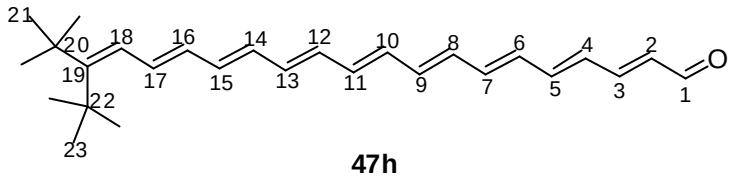
General procedure 1

0.190 g (0.58 mmol) **47f** in 7 mL of THF; 0.630 g (1.47 mmol) **141** in 15 mL of THF; 0.158 g (1.407 mmol) *t*-BuOK; 0.517 g (4.10 mmol) oxalic acid in 4.10 mL of water. Product was purified by column chromatography on silica gel with CH_2Cl_2: 0.180 g (0.52 mmol, 90%), red solid.

R_F (CH_2Cl_2): 0.57.
M.p. 141-143 °C.
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.23, 1.37 (s, 18 H, 19/21-H), 6.08 (d, 1 H, $^3J_{16\text{-H},\ 15\text{-H}}$ = 11.8 Hz, 16-H), 6.12-6.18 (m, 2 H, 12/14-H), 6.25-6.57 (m, 9 H, 4/6/7/8/9/10/11/12/13-H), 6.72 (dd, 1 H, $^3J_{5\text{-H},\ 6\text{-H}}$ = 11.2 Hz and $^3J_{5\text{-H},\ 4\text{-H}}$ = 14.6 Hz, 5-H), 6.89 (dd, 1 H, $^3J_{15\text{-H},\ 16\text{-H}}$ = 11.6 Hz, $^3J_{15\text{-H},\ 14\text{-H}}$ = 13.0 Hz, 15-H), 7.14 (dd, 1 H, $^3J_{3\text{-H},\ 4\text{-H}}$ = 11.3 Hz, $^3J_{3\text{-H},\ 2\text{-H}}$ = 15.0 Hz, 3H), 9.56 (d, 1 H, $^3J_{1\text{-H},\ 2\text{-H}}$ = 7.9 Hz, 1-H).
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 193.37 (d, C-1), 158.78 (s, C-17), 151.76 (d, C-3), 142. 76 (d, C-5), 139. 05 (d, C-15), 136.96, 135.81, 135.46, 133.94, 132.19, 132.16, 132.02, 131.91, 131.37, 130.66, 129.62 (d, C-2/4/6/7/8/9/10/11/12/13/14), 123.98 (d, C-16), 39.04, 37.98 (s, C-18/20), 33.75, 31.70 (q, C-19/21).
IR (KBr): $\tilde{n}$ = 2957 cm^{-1} (m), 1668 (C=O, s), 1600 (m), 1532 (C=C, s), 1482 (w), 1367 (w), 1216 (w), 1139 (s), 1104 (m), 1109 (vs).
UV ($CHCl_3$): λ_{max} (lg ε) = 444 nm (4.83)

During spectrometric analysis the compound polymerized.

4.3.14: 19-(*tert*-Butyl)-18,18-dimethyl-2,4,6,8,10,12,14,16-unododecanonaenal (47h)



47h

To a stirred suspension of 0.550 g (1.29 mmol) phosphonium salt **141** in anhydrous THF (30 mL) was added 0.140 g (1.23 mmol) *t*-BuOK under N_2. An immediate colour change from white to yellow was observed. After stirring for 30 min 0.180 g (0.514 mmol) aldehyde **47g** in THF (20 mL) was added dropwise and the reaction mixture was refluxed for 6 h. After cooling to room temp. 7 equivalents of aqueous oxalic acid solution was added and the reaction was left stirring overnight. After the phases were separated the aqueous phase was extracted several times with Et_2O. The combined organic phases were neutralized with saturated $NaHCO_3$ solution and, after the phase separation, dried with anhydrous $MgSO_4$. The solvent was removed in a rotary evaporator and the remaining residue was purified by column chromatography on silica gel using ethylacetate. The dark red coloured, highly unsoluble aldehyde **47h** was obtained in 60% yield (0.116 g, 3.08 mmol).

R_F (EtOAc): 0.25.

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.22, 1.32 (s, 18 H, 21/23-H), 6.05-6.51 (m, 14 H, 2/4/6/7/8/9/10/11/12/13/14/15/16/18-H), 6.66-6.95 (m, 2 H, 5/17-H), 7.13-7.26 (dd, 1 H, $^3J_{3\text{-H, }2\text{-H}}$ = 15 Hz, $^3J_{3\text{-H, }4\text{-H}}$ = 11.1 Hz, 3-H), 9.58 (d, 1 H, H-1).

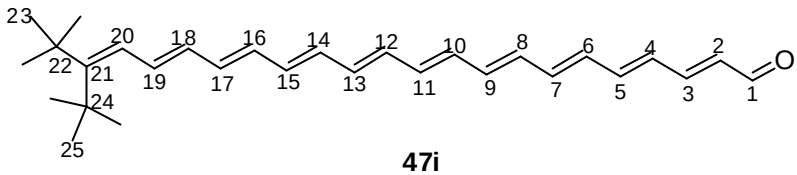
IR (KBr): $\tilde{n}$ = 2956 cm^{-1} (w), 1669 (C=O, s), 1612 (w), 1523 (C=C, s), 1463 (w), 1392 (w), 1216 (w), 1132 (m), 1010 (vs).

UV ($CHCl_3$): λ_{max} (lg ε) = 456 nm (4.87), 472 (4.84, sh).

The aldehyde **47h** could not be characterized fully. In the NMR solvent ($CDCl_3$) an immediate colour change from dark red to greenish-brown with the disappereance of the

signal due to aldehyde proton (H-1) was observed. During the mass spectrometric measurements **47h** polymerized. However, the existence of the compound was proven by the subsequent Knoevenagel condensation with malononitrile to **167**, which could be characterized (see Exp. 4.3.33).

4.3.15: 21-(*tert*-Butyl)-20,20-dimethyl-2,4,6,8,10,12,14,16,18-tridodecaundocaaenal (47i)



47i

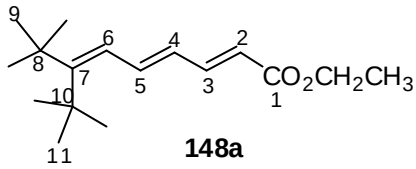
To a stirred suspension of 199 mg (0.465 mmol) phosphonium salt **141** in anhydrous THF (20 mL) was added 50 mg (0.464 mmol) *t*-BuOK under N_2. An immediate colour change from white to yellow was observed. After stirring for 30 min 70 mg (0.186 mmol) aldehyde **47h** in THF (35 mL) was added dropwise and the reaction mixture was refluxed for 6 h. During reflux insoluble dark red coloured crystals were observed in the reaction flask (probably undissolved starting material **47h)**. After cooling the mixture to room temp. 7 equivalents of aqueous oxalic acid solution was added and the reaction was left stirring overnight. After the phases had been separated, the aqueous phase was extracted several times with Et_2O. The combined organic phases were neutralized with saturated $NaHCO_3$ solution and dried with anhydrous $MgSO_4$. The solvent was removed in a rotary evaporator and the remaining residue was purified by column chromatography on silica gel using ethylacetate. The very dark red coloured and extremely unsoluble aldehyde **47i** was obtained in 53% yield (70 mg, 0.100 mmol).

R_F (EtOAc) 0.23

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.23, 1.37 (s, 18 H, 23/25-H), 6.10-6.95 (m, 18 H, 2/4/5/6/7/8/9/10/11/12/13/14/15/16/17/18/19/20-H), 7.11-7.23 (dd, 1 H, H-3), 9.61 (d, 1 H, H-1)
UV ($CHCl_3$): λ_{max} (lg ε) = 468 nm (4.81)

The aldehyde **47i** could not be characterized fully. During mass spectrometric analysis it polymerized. In the NMR solvent ($CDCl_3$) an immediate colour change from dark red to greenish-brown with the disappereance of the signal of aldehyde proton (H-1) was observed. The compound has to be used quickly for further Knoevenagel condensation with malononitrile leading to **168** (see Exp. 4.3.34).

4.3.16: all-*trans*-7-*tert*-Butyl-8,8-dimethyl-nona-2,4,6-trienoic acid ethyl ester(148a)



148a

General procedure 2

0.66 g (6.55 mmol) diisopropyl amine in 20 mL of THF at −78 °C; 4.1 mL (6.55 mmol) n-BuLi; 1.63 g (6.55 mmol) **147** in 10 mL of THF; 1.00 g (5.95 mmol) **114**.

Product **148a** was purified by column chromatography on silica gel with ethylacetate/ hexane = 1/10 (v/v): 1.41 g (5.35 mmol, 96%), colourless oil.

R_F (EtOAc/hexane = 1:10): 0.52.

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.16, 1.31 (s, 18 H, 9/11-H), 1.19 (t, 3 H, CH_3), 4.13 (q, 2 H, CH_2), 5.76 (d, 1 H, $^3J_{2\text{-H, }3\text{-H}}$ = 15.3 Hz, 2-H), 6.00-6.16 (m, 2 H, 4/6-H), 7.07 - 7.25 (dd, 1 H, $^3J_{5\text{-H, }4\text{-H}}$ = 14.4 Hz and $^3J_{5\text{-H, }6\text{-H}}$ = 11.0 Hz, 5-H), 7.30-7.38 (dd, 1 H, $^3J_{3\text{-H, }2\text{-H}}$ = 15.2 Hz and $^3J_{3\text{-H, }4\text{-H}}$ = 11.3 Hz, 3-H).

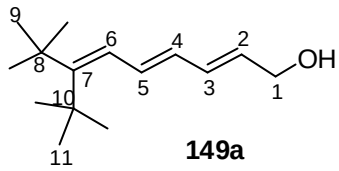
^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 167.24 (s, C-1), 162.70 (s, C-7), 145.09 (d, C-3), 140.26 (d, C-5), 129. 06 (d, C-4), 123.33 (d, C-6), 119.60 (d, C-2), 60.14 (t, CH_2), 39.26, 38.18 (s, C-7/8), 33.91, 31.57 (q, 9/11), 14.29 (q, CH_3).

IR (KBr): $\tilde{n}$ = 3000 cm^{-1} (b), 2958 (vs), 1715 (C=O, w), 1607 (m), 1484 (m), 1367 (m), 1217 (m), 1136 (m), 1035 (m), 991 (m).

MS (GC-MS): *m/z* (%) = 264 [M^+], 219, 208 [M^+-$C(CH_3)_3$+1] (35), 180 (15), 161 (50), 147 (20), 133 (100), 119 (30), 107 (50), 91 (20), 70 (10), 69 (10), 57 [$C(CH_3)_3$] (90).

UV ($CHCl_3$): λ_{max} (lg ε) = 248 nm (3.97), 280 (4.26), 288 (4.31), 294 (4.28), 314 (3.79), 332 (3.61).

4.3.17: all-*trans*-7-*tert*-Butyl-8,8-dimethyl-nona-2,4,6-trien-1-ol (149a)



149a

General procedure 3

0.60 g (2.27 mmol) **148a** in 20 mL of toluene; 5.68 mL (5.675 mmol) of DIBAL; 0.65 mL of 50% aq. CH_3COOH.

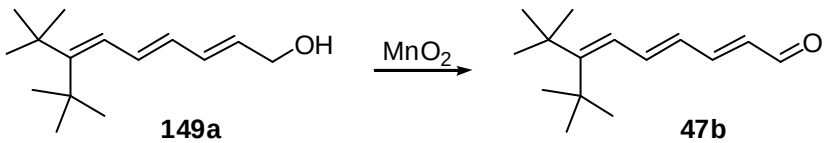
Purification of the alcohol **149a** on silica gel was observed to cause immediate polymerization. The compound was quite unstable and it had to be used rapidly for further reaction (Exp. 4.3.18). Because of its high instability the compound could not be characterized fully: 0. 377 g (1.70 mmol, 75%), colourless oil.

R_F (EtOAc/hexane = 1:2.5): 0.61.

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.22, 1.36 (s, 18 H, 9/11-H), 2.35 (s, 1 H, OH), 4.20 (d, 2 H, $^3J_{1\text{-H, }2\text{-H}}$ = 6.6 Hz, 1-H), 5.74-5.94 (m, 1 H, 2-H), 6.00-6.14 (m, 2 H, 4/6-H), 6.77-6.90 (dd, 1 H, $^3J_{5\text{-H, }4\text{-H}}$ = 14.2 Hz and $^3J_{5\text{-H, }6\text{-H}}$ = 11.9 Hz, 5-H), 7.14-7.25 (dd, 1 H, $^3J_{3\text{-H, }2\text{-H}}$ = 14. Hz and $^3J_{3\text{-H, }4\text{-H}}$ = 13.1 Hz, 3-H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 157.78 (s, C-7), 132.98, 132.21, 130.85, 130.82 (d, C-3/4/5/6), 123.45 (d, C-2), 63.52 (t, C-1), 38.90, 37.80 (s, C-8/10), 33.70, 31.74 (q, C-9/11).

4.3.18: Oxidation of 149a to the aldehyde 47b with MnO_2



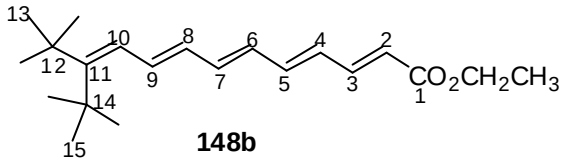
149a **47b**

A suspension of 4.08 g (47 mmol) MnO_2 and 0.350 g (1.57 mmol) of **149a** in CH_2Cl_2 (30 mL) was stirred for 3 h. The mixture was filtered through celite, then through silica gel using CH_2Cl_2 as the eluent. After evaporation of solvent the residue was purified by column chromatography on silica gel with ethylacetate/hexane = 1:10 (v/v) as the eluent: 0.232 g (1.06 mmol, 67%) **47b** as a yellow oil.

Because the alcohol **149a** was directly used without further purification (see Exp. 4.3.17) the 67% yield cannot be considered as the exact yield of this reaction. The overall yield for the conversion of aldehyde **114** to **47b** was 51% (Exp. 4.3.16, Exp. 4.3.17, Exp. 4.3.18).

The spectral data of the compound **47b** are in accordance with the data given in the ref.[23b]

4.3.19: all-*trans*-11-*tert*-Butyl-12,12-dimethyl-trideca-2,4,6,8,10-pentaenoic acid ethyl ester (148b)



148b

General procedure 2

0.172 g (1.70 mmol) diisopropyl amine in 10 mL of THF at –78 °C ; 1.06 mL (1.70 mmol) n-BuLi; 0.430 g (1.70 mmol) of **147** in 10 mL of THF; 0.340 g (1.55 mmol) **47b**.

Product **148b** was purified by column chromatography on silica gel with ethylacetate/hexane = 1/10 (v/v): 0.423 g (1.34 mmol, 87%), yellow, low melting (10-15°C) solid.

R_F (EtOAc/hexane = 1:10): 0.44.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.29 (t, 3 H, CH_3), 1.23, 1.37 (s, 18 H, 13/15-H), 4.20 (q, 4 H, CH_2), 5.85 (d, 1 H, $^3J_{2\text{-H, }3\text{-H}}$ = 15.2 Hz, 2-H), 6.07 - 6.15 (m, 2 H, 8/10-H), 6.18-6.34 (m, 2 H, 4/6-H), 6.51 - 6.69 (m, 2 H, 5/7-H), 6.92 - 6.98 (dd, $^3J_{9\text{-H, }8\text{-H}}$ = 14.7 Hz and $^3J_{9\text{-H, }10\text{-H}}$ = 12.0 Hz, 1H, 9-H), 7.29 - 7.36 (dd, 1 H, $^3J_{3\text{-H, }2\text{-H}}$ = 15.1 Hz and $^3J_{3\text{-H, }4\text{-H}}$ = 11.5 Hz, 3-H).

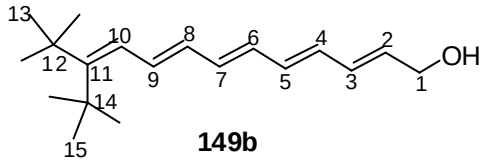
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.18 (s, C-1), 159.74 (s, C-11), 144.55 (d, C-3), 140.97, 137.99 (d, C-5/7), 135.33 (d, C-9), 131.72 (d, C-8), 130.90 (d, C-4), 129.41 (d, C-6), 123.94 (d, C-10), 120.22 (d, C-2), 60.23 (t, CH_2), 39.13, 38.07 (s, C-12/14), 3.85, 31.73 (q, C-13/15), 14.31 (q, CH_3).

IR (KBr): $\tilde{n}$ = 3059 cm^{-1} (m), 2959 (s), 1704 (C=O, vs), 1625 (m), 1572 (m), 1465 (m), 1448 (m), 1368 (m), 1307 (m), 1246 (s), 1141 (vs), 1127 (vs), 1012 (vs).

MS (70 eV): *m*/*z* (%) = 316 [M^+] (10), 259 [M^+-$C(CH_3)_3$] (20), 185 (10), 159 (13), 149 (12), 133 (16), 127 (10), 111 (18), 197 (15), 91 (16), 83 (13), 73 (21), 69 (14), 57 [$C(CH_3)_3$] (100).

UV ($CHCl_3$): λ_{max} (lg ε) = 296 nm (3.90), 370 (4.36), 384 (4.32), 392 (4.25).

4.3.20: all-*trans*-11-*tert*-Butyl-12,12-dimethyl-trideca-2,4,6,8,10-pentaen-1-ol (149b)



149b

General procedure 3

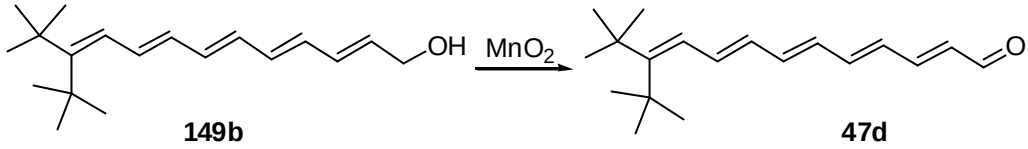
0.93 g (2.94 mmol) of **148b** in 25 mL of toluene; 8.83 mL (8.83 mmol) of DIBAL; 1.00 mL of 50% aq. CH_3COOH.

The alcohol **149b** was highly unstable and it had to be used quickly for further reaction (Exp. 4.3.21). Because of its high instability the compound could not be characterized fully. Crude mixture: 0. 830 g (100%), light yellow oil.

R_F (EtOAc/hexane = 1:2.5): 0.43.

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.09, 1.24 (s, 18 H, 13/15-H), 4.07 (d, 2 H ^3J = 5.46 Hz, 1-H), 5.6 - 6.3 (m, 8 H), 6.65 - 6.71 (m, 1 H).

4.3.21: Oxidation of the alcohol 149b to the aldehyde 47d with MnO_2



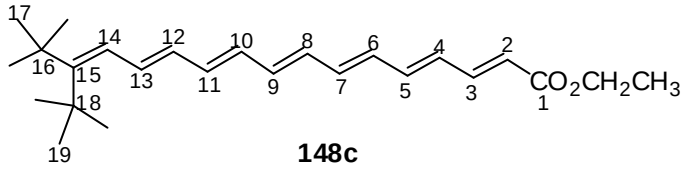
149b **47d**

A mixture of 10.22 g (117 mmol) of MnO_2 and 0.800 g of crude **149b** (see Exp. 4.3.20) in CH_2Cl_2 (65 mL) was stirred for 3 h. The mixture was filtered first through celite, then through silica gel using CH_2Cl_2 as the eluent. After evaporation of the solvent the remaining residue was purified by column chromatography on silica gel using ether/ petrolether = 3:10 (v/v) as the eluent: 0.348 g (1.27 mmol) **47b** .

Because the alcohol **149b** was directly used without further purification the exact yield of this reaction cannot be given. But the overall yield of conversion of aldehyde **47b** to **47d** was 51% (Exp. 4.3.19, Exp. 4.3.20, Exp. 4.3.21).

The spectral data of **47d** are in accordance with the data given in ref.[23b]

4.3.22: all-*trans*-15-*tert*-Butyl-16,16-dimethyl-heptadeca-2,4,6,8,10,12,14-heptaenoic acid ethyl ester (148c)



148c

General procedure 2.

0.250 g (2.48 mmol) of diisopropyl amine in 15 mL of THF at −78 °C ; 1.55 mL (2.48 mmol) of n-BuLi; 0.620 g (2.48 mmol) of **147** in 10 mL of THF; 0.450 g (1.64 mmol) of **47d**. Product **148c** was purified by column chromatography on silica using ethylacetate/hexane = 1:2.5 (v/v): 0.540 g (1.47 mmol, 90%), orange solid.

R_F (EtOAc/hexane = 1:2.5): 0.83.

M.p. 98°C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.15, 1.30 (s, 18 H, 17/19-H), 1.20 (t, 3H, CH_3), 4.13 (q, 2 H, CH_2), 5.78 (d, 1 H, $^3J_{2\text{-H, }3\text{-H}}$ = 15.2 Hz, 2-H), 6.01 (d, 1 H, $^3J_{14\text{-H, }13\text{-H}}$ = 11.7 Hz, H-14), 6.07 (dd, 1 H, $^3J_{12\text{-H, }13\text{-H}}$ = 14.1 Hz and $^3J_{12\text{-H, }11\text{-H}}$ =11.1 Hz, H-12), 6.17-6.42 (m,

6 H, 4/5/8/7/8/9/10-H), 6.53 (dd, 1 H, $^3J_{11\text{-H, }10\text{-H}}$ = 14.4 Hz and $^3J_{11\text{-H, }12\text{-H}}$ = 11.1 Hz, 11-H), 6.82 (dd, 1 H, $^3J_{13\text{-H, }12\text{-H}}$ = 14.1 Hz and $^3J_{13\text{-H, }14\text{-H}}$ = 11.7 Hz, 13-H), 7.25 (dd, 1 H, $^3J_{3\text{-H, }2\text{-H}}$ = 15.2 Hz and $^3J_{3\text{-H, }4\text{-H}}$ = 11.6 Hz, 3-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.17 (s, C-1), 158.78 (s, C-15), 144.40 (d, C-3), 140.79, 137.47 (d, C-11/9), 135.98, 135.53, 133.99, 132.17, 132.04, 131.87, 131.60, 129.75 (d, C-4/5/6/7/8/10/12/13), 124.04 (d, C-14), 120.04 (d, C-2), 60.21 (t, CH_2), 39.09, 38.03 (s, C-16/18), 33.82, 31.78 (q, C-17/19), 14.32 (q, CH_3).

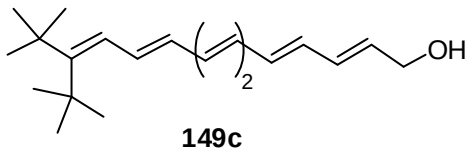
IR (KBr): $\tilde{n}$ = 3000 cm^{-1} (b), 2958 (m), 1708 (C=O, s); 1621 (m), 1547 (m), 1367 (m), 1301 (m), 1267 (m), 1217 (m), 1139 (s), 1012 (vs).

MS (70 eV): *m/z* (%) = 368 [M^+] (86), 311 [M^+-$C(CH_3)_3$] (92), 284 (20), 259 (10), 237 (14), 223 (12), 211 (11), 197 (17), 189 (16), 165 (27), 159 (26), 145 (26), 129 (27), 117 (31), 109 (27), 91 (41), 79 (22), 57 [$C(CH_3)_3$] (100), 55 (22), 43 (20).

UV ($CHCl_3$): λ_{max} (lg ε) = 238 nm (4.08), 312 (3.89), 378 (4.35), 400 (4.54, sh), 420 (4.62), 436 (4.56, sh).

Elemental Analysis $C_{25}H_{36}O_2$ (368.6) Calc. C 81.46% H 9.85%
Found C 79.78% H 9.89%

4.3.23: all-*trans*-15-*tert*-Butyl-16,16-dimethyl-heptadeca-2,4,6,8,10,12,14-heptaen-1-ol (149c)



149c

General procedure 3

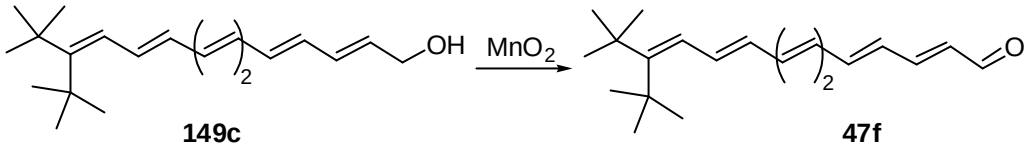
0.300 g (0.815 mmol) of **148c** in 25 mL of toluene; 2.31 mL (2.31 mmol) of DIBAL; 0.26 mL of 50% aq. CH_3COOH.

The alcohol **149c** was extremely unstable and it had to be used quickly for further reaction (Exp. 4.3.24).

Crude mixture: 0.250g (93%), yellow oil.

R_F (EtOAc/hexane = 1:2.5): 0.28.

4.3.24: Oxidation of 149c to the aldehyde 47f with MnO_2



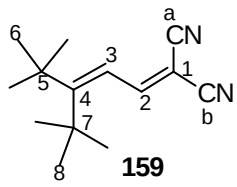
149c **47f**

A suspension of 2.83g (32 mmol) MnO_2 and 0.250 g of crude alcohol **149c** (see Exp. 6.8) in CH_2Cl_2 (30 mL) was stirred for 3 h. The mixture was filtered first through celite, then through silica gel using CH_2Cl_2 as the eluent. After evaporation of the solvent the remaining residue was purified by column chromatography on silica gel using CH_2Cl_2 as the eluent: 0.122 g (0.037 mmol) **47f** .

Because the alcohol **149c** was directly used without further purification the exact yield of this reaction cannot be given. The overall yield of conversion of the aldehyde **47d** to **47f** was 46% (Exp. 4.3.22, Exp. 4.3.23, Exp. 4.3.24).

The spectral data of **47f** are in accordance with the data given Exp. 4.3.12.

4.3.25: 2-(3-*tert*-Butyl-4,4-dimethyl-pent-2-enylidne)-malononitrile (159)



159

General procedure 4

0.60 g (3.57 mmol) of **114**; 0.24 g (3.57 mmol) of malononitrile; 3 mg (0.032 mmol) of β-alanine in 1.20 mL of 95% EtOH.

Product **159** was purified by recrystallization from hexane: 0.75 g (3.45 mmol, 96%), colourless plates.

R_F (EtOAc/hexane = 1:7): 0.60.

M.p. 84-85 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.25, 1.36 (s, 18 H, 7/12-H), 6.56 (d, 1 H, $^3J_{3\text{-H, }2\text{-H}}$ = 12.6 Hz, 3-H), 8.16 (d, 1 H, $^3J_{2\text{-H, }3\text{-H}}$ = 12.6 Hz, 2-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 182.05 (s, C-4), 158.17 (d, C-2), 119.57 (d, C-3), 114.00, 111.40 (s, C-a/b), 82.36 (s, C-1), 39.96, 41.37 (s, C-5/7), 31.06, 34.77 (q, C-6/8).

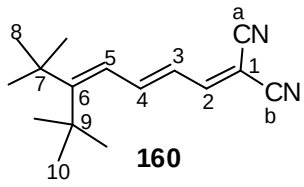
IR (KBr): $\tilde{n}$ = 2997 cm^{-1} (CH, s), 2226 (C≡N, s), 1585 (C=C, s), 1484 (m), 1370.3 (m), 1216 (m).

MS (70 eV): *m/z* (%) = 217 [M^++1] (10), 216 [M^+] (20), 207 (20), 201 [M^+- CH_3] (100), 195 (18), 160 [M^+- $C(CH_3)_3$] (20), 145 (17), 84 (12), 57 [$C(CH_3)_3$] (100).

UV ($CHCl_3$): λ_{max} (lg ε) = 318 nm (4.08).

Elemental Analysis $C_{14}H_{20}N_2$ (216.3) Calc. C 77.73% H 9.32% N 12.95%
Found C 77.74% H 9.39% N 12.90%

4.3.26: 2-(5-*tert*-Butyl-6,6-dimethyl-hepta-2,4-dienylidne)-malononitrile (160)



160

General procedure 4

1.15 g (5.93 mmol) of **47a**; 0.39 g (5.93 mmol) of malononitrile; 5 mg (0.053 mmol) of β-alanine in 2.40 mL of 95% EtOH.

Product **160** was purified by recrystallization in hexane: 1.40 g (5.78 mmol, 97%), yellow needles.

R_F (EtOAc/hexane = 1:7): 0.44.

M.p. 110-113 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.26 (s, 9 H, 10-H), 1.40 (s, 9 H, 8-H), 6.25 (d, 1 H, $^3J_{5\text{-H, }4\text{-H}}$ = 12.1 Hz, 5-H), 6.56 (dd, 1 H, $^3J_{3\text{-H,}2\text{-H}}$ = 11.7 Hz and $^3J_{3\text{-H,}4\text{-H}}$ = 14.0 Hz, 3-H), 7.52 (d, 1 H, $^3J_{2\text{-H,}3\text{-H}}$ = 11.7 Hz, 2-H), 7.63 (dd, 1 H, $^3J_{4\text{-H,}5\text{-H}}$ = 12.0 Hz and $^3J_{4\text{-H,}5\text{-H}}$ = 14.0 Hz, 4-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 173.95 (s, C-6), 160.16 (d, C-2), 149.39 (C-4), 125.66 (d, C-3), 123.51 (d, C-5), 113.94, 112.05 (s, C-a/b), 80.85 (s, C-1), 40.38, 39.26 (s, C-7/9), 34.45 (q, C-10), 31.34 (q, C-8).

IR (KBr): $\tilde{n}$ = 2956 cm^{-1} (CH, m), 2225 (C≡N, m), 1574 (C=C, s), 1372 (w), 1204 (m), 1175 (m), 997 (m).

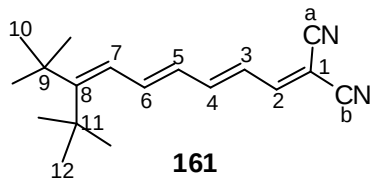
MS (70 eV): *m/z* (%) = 242 [M^+] (1.4), 227 [M^+- CH_3] (0,8), 186 [M^+-$C(CH_3)_3$] (50), 171 (90), 157(10), 143 (10), 84 (38), 57 [$C(CH_3)_3$] (100).

UV ($CHCl_3$): λ_{max} (lg ε) = 374 nm (4.60).

Elemental Analysis $C_{16}H_{22}N_2$ (242.4) Calc. C 79.29% H 9.15% N 11.56%

Found C 79.29% H 9.22% N 11.48%

4.3.27: 2-(7-*tert*-Butyl-8,8-dimethyl-nona-2,4,6-trienylidne)-malononitrile (161)



161

General procedure 4.

1.00 g (4.55 mmol) of **47b**; 0.30 g (4.55 mmol) of malononitrile; 3.0 mg (0.041 mmol) of β-alanine in 2.40 mL of 95% EtOH.

Product **161** was purified by recrystallization from hexane: 1.10 g (4.10 mmol, 90%), orange plates.

R_F (EtOAc/hexane = 1:7): 0.41.

M.p. 160-161 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.26, 1.40 (s, 18 H, 10/12-H), 6.19 (d, 1 H, $^3J_{7\text{-H, }6\text{-H}}$ = 11.9 Hz, 7-H), 6.28 (dd, 1 H, $^3J_{5\text{-H, }4\text{-H}}$ = 11.3 Hz and $^3J_{5\text{-H, }6\text{-H}}$ = 11.3 Hz, 5-H), 6.70 (dd, 1 H, $^3J_{3\text{-H, }2\text{-H}}$ = 11.8 Hz and $^3J_{3\text{-H, }4\text{-H}}$ = 11.9 Hz, 3-H), 7.05 (dd, 1 H, $^3J_{4\text{-H, }5\text{-H}}$ = 11.3 Hz and $^3J_{4\text{-H, }3\text{-H}}$ = 11.8 Hz, 4-H), 7.38 (dd, 1 H, $^3J_{6\text{-H, }7\text{-H}}$ = 11.3 Hz and $^3J_{6\text{-H, }5\text{-H}}$ = 11.9 Hz, 6-H), 7.42 (d, 1 H, $^3J_{2\text{-H, }3\text{-H}}$ = 11.7 Hz, 2-H)

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.77 (s, C-8), 159.34 (d, C-2), 150.97 (d, C-4), 144.50 (d, C-6), 130.05 (d, C-3), 124.87, 123.84 (d, C-5/7), 114.09, 112.05 (s, C-a/b), 80.27 (s, C-1), 39.77, 38.71 (s, C-9/11), 31.43, 34.13 (q, C-10/12).

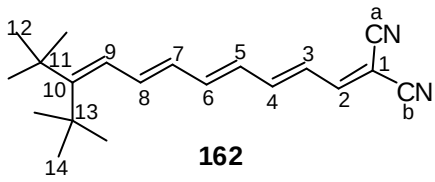
IR (KBr): $\tilde{n}$ = 2959 cm^{-1} (CH, w) , 2227 (C≡N, m), 1590 (m), 1558 (s, C=C), 1196 (w), 1170 (m), 1008 (m)

MS (70 eV): *m/z* (%) = 268 [M^+] (4), 212 (50), 196 (20), 184 (24), 169 (22), 157 (10), 143 (30), 57 [$C(CH_3)_3$] (100).

UV ($CHCl_3$): λ_{max} (lg ε) = 276 nm (3.64), 314 (3.71), 422 (4.70)

Elemental Analysis $C_{18}H_{24}N_2$ (268.4) Calc. C 80.55% H 9.01% N 10.44%
Found C 80.43% H 9.09% N 10.36%

4.3.28: 2-(9-*tert*-Butyl-10,10-dimethyl-undeca-2,4,6,8-tetraenylidne)-malononitrile (162)



162

General procedure 4

0.468 g (1.90 mmol) of **47c**; 0.125 g (1.90 mmol) of malononitrile; 1.5 mg (0.017 mmol) of β-alanine in 1.50 mL of 95% EtOH.

Product **162** was purified by recrystallization from hexane: 0.500 g (1.70 mmol, 90%), red plates.

R_F (EtOAc/hexane = 1:7): 0.39.

M.p. 161-163 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.25 (s, 9 H, H-12), 1.39 (s, 9 H, 14-H), 6.15 (d, 1 H, $^3J_{9\text{-H, }8\text{-H}}$ = 11.8 Hz, 9-H), 6.25 (dd, 1 H, $^3J_{7\text{-H, }8\text{-H}}$ = 14.0 Hz, $^3J_{7\text{-H, }6\text{-H}}$ = 11.5 Hz, 7-H), 6.43 (m, 1 H, 5-H), 6.70 (m, 1 H, 3-H), 6.80 (m, 1 H, 6-H), 6.96 (dd, 1 H, $^3J_{4\text{-H, }3\text{-H}}$ = 14.3 Hz, $^3J_{4\text{-H, }5\text{-H}}$ = 11.4 Hz, 4-H), 7.19 (m, 1 H, 8-H), 7.43 (d, 1 H, $^3J_{2\text{-H, }3\text{-H}}$ = 12.0 Hz, 2-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 164.26 (s, C-10), 159.16 (d, C-2), 150.30 (d, C-4), 145.90 (d, C-6), 140.14 (d, C-8), 131.12, 129.56 (d, C-5/7), 125.11, 123.90 (d, C-3/9), 114.14, 112.15 (s, C-a/b), 80.30 (s, C-1), 39.49, 38.42 (s, C-11/13), 33.98, 31.54 (q, C-12/14).

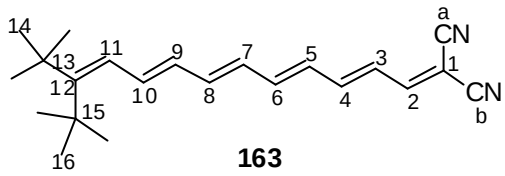
IR (KBr): $\tilde{n}$ = 2956 cm^{-1} (CH, w), 2227 (C≡N, m), 1552 (C=C, s), 1519 (s), 1183 (m), 1150 (m), 1012 (s).

MS (70 eV): *m/z* (%) = 295 [M^++1] (4), 294 [M^+] (19), 238 (64), 237 [M^+- $C(CH_3)_3$] (84), 222 (20), 210 (42), 199 (40), 155 (18), 143 (18), 131 (20), 120 (14), 105 (20), 91 (20), 77 (12), 57 [$C(CH_3)_3$] (100).

UV ($CHCl_3$): λ_{max} (lg ε) = 296 nm (3.73), 442 (4.73, sh), 464 (4.80).

Elemental Analysis $C_{20}H_{26}N_2$ (294.4) Calc. C 81.59% H 8.90% N 9.51%
Found C 81.53% H 8.90% N 9.57%

4.3.29: 2-(11-*tert*-Butyl-12,12-dimethyl-trideca-2,4,6,8,10-pentaenylidne)-malononitrile (163)



163

General procedure 4.

0.200 g (7.35 mmol) of **47d**; 0.049 g (7.35 mmol) of malononitrile; 0.6 mg (0.007 mmol) of β-alanine in 1.50 mL of 95% EtOH.

Product **163** was purified from recrystallization in hexane: 0.220 g (6.87 mmol, 93%), black plates.

R_F (EtOAc/hexane = 1:7): 0.38.

M.p. 163-165 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.24, 1.39 (s, 18 H, 14/16-H), 6.12 (d, 1 H, $^3J_{11\text{-H, }10\text{-H}}$ = 11.9 Hz, 11-H), 6.21 (dd, 1 H, $^3J_{9\text{-H, }10\text{-H}}$ = 14.3 Hz, $^3J_{9\text{-H, }8\text{-H}}$ = 11.3 Hz, 9-H), 6.33 - 6.45 (m, 2 H, 5/7-H), 6.62 - 6.78 (m, 3 H, 3/6/8-H), 6.96 (dd, 1 H, $^3J_{4\text{-H, }3\text{-H}}$ = 14.30 Hz, $^3J_{4\text{-H, }5\text{-H}}$ = 11.5 Hz, 4-H), 7.04 (dd, 1 H, $^3J_{10\text{-H, }9\text{-H}}$ = 14.1 Hz, $^3J_{10\text{-H, }11\text{-H}}$ = 12.0 Hz, 10-H), 7.42 (d, 1 H, $^3J_{2\text{-H, }3\text{-H}}$ = 11.9 Hz, 2-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 162.02 (s, C-12), 159.00 (d, C-2), 150.20 (d, C-4), 145.35 (d, C-6), 141.42 (d, C-8), 137.64 (d, C-10), 131.56, 130.81, 129.27 (d, C-3/5/7),

125.12 (d, C-9), 123.94 (d, C-11), 114.19, 112.17 (s, C-a/b), 79.96 (s, C-1), 39.30, 38.24 (s, C-13/15), 33.89, 31.61 (q, C-14/16).

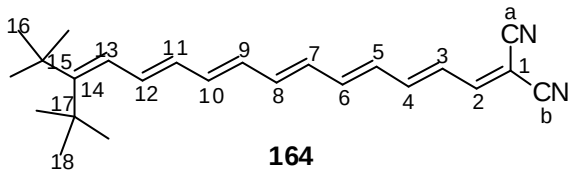
IR (KBr): $\tilde{n}$ = 2957 cm^{-1} (CH, w), 2221 (C≡N, m), 2214 (m), 1532 (C=C, s), 1513 (s), 1217 (w), 1164 (m), 1144 (m), 1005(m).

MS (70 eV): *m/z* (%) = 321 [M^++1] (6), 320 [M^+] (20), 264 (50), 263 [M^+- $C(CH_3)_3$] (100), 238 (18), 221 (12), 143 (10), 131 (10), 115 (10), 105 (10), 57 [$C(CH_3)_3$] (40).

UV ($CHCl_3$): λ_{max} (lg ε) = 282 nm (4.17), 342 (3.80, sh), 484 (4.74), 498 (4.74)

Elemental Analysis $C_{22}H_{28}N_2$ (320.5) Calc. C 82.45% H 8.81% N 8.74%
Found C 80.92% H 8.82% N 9.55%

4.3.30: 2-(13-*tert*-Butyl-14,14-dimethyl-pentadeca-2,4,6,8,10,12-hexaenylidne)-malononitrile (164)



164

General procedure 4.

30 mg (0.093 mmol) of **47e**; 6 mg (0.093 mmol) of malononitrile; 0.1 mg (0.0011 mmol) of β-alanine in 4 mL of 95% EtOH.

Product **164** was purified by recrystallization from hexane: 33 mg (0.088 mmol, 95%), black plates.

R_F (EtOAc/hexane = 1:7): 0.36.

M.p. 169-170 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.23 (s, 9 H, 16-H), 1.38 (s, 9 H, 18-H), 6.10 (d, 1 H, $^3J_{13\text{-H, }12\text{-H}}$ = 11.8 Hz, 13-H), 6.18 (dd, 1 H, $^3J_{11\text{-H, }12\text{-H}}$ = 14.4 Hz, $^3J_{11\text{-H, }10\text{-H}}$ = 11.3 Hz, 11-H), 6.30-6.45 (m, 3 H, 5/7/9-H), 6.52 - 6.79 (m, 4 H, 3/6/8/10-H), 6.92 - 7.02 (m, 2H, 4/12-H), 7.41 (d, 1 H, $^3J_{2\text{-H, }3\text{-H}}$ = 12.0 Hz, 2-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 160.64 (s, C-14), 158.91 (d, C-2), 150.06 (d, C-4), 145.26 (d, C-6), 140.94 (d, C-12), 138.83 (d, C-8),136.02 (d, C-10), 131.84, 131.32,

131.27, 130.13, 125.31 (d, C-3/5/7/9/11), 123.95 (d, C-13), 114.07, 111.77 (s, C-a/b), 79.96 (s, C-1), 39.19, 38.13 (s, C-15/17), 33.83 (q, C-16), 31.62 (q, C-18).

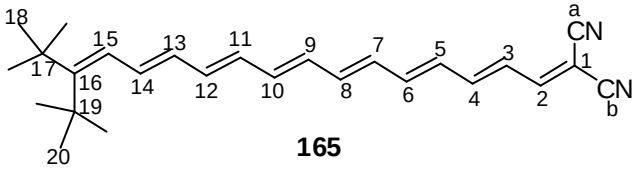
IR (KBr): $\tilde{n}$ = 2952 cm^{-1} (CH, w), 2220 (C≡N, m), 1532 (C=C, s), 1516 (s), 1485 (w), 1218 (w), 1136 (s), 1008 (s).

MS (70 eV): *m*/*z* (%) = 347 [M^++1] (8), 346 [M^+] (30), 2990 (34), 289 [M^+- $C(CH_3)_3$] (100), 263 (6), 262 (30), 247 (12), 181 (10), 169 (20), 143 (26), 131 (20), 115 (26), 105 (15), 91 (24), 79 (10), 77 (12), 57 [$C(CH_3)_3$] (46).

UV ($CHCl_3$): λ_{max} (lg ε) = 304 nm (4.31), 478 (4.75), 512 (4.86), 532 (4.83).

Elemental Analysis $C_{26}H_{28}N_2$ (346.5) Calc. C 83.82% H 8.66% N 7.52%
Found C 76.93% H 8.11% N 7.09%

4.3.31: 2-(15-*tert*-Butyl-16,16-dimethyl-heptadeca-2,4,6,8,10,12,14-heptaenylidne)-malononitrile (165)



165

General procedure 4

30 mg (0.092 mmol) of **47f**; 6 mg (0.092 mmol) of malononitrile; 0.1 mg (0.0011 mmol) of β-alanine in 4 mL of 95% EtOH.

Product **165** was purified by recrystallization from hexane: 30 mg (0.080 mmol, 87%), black crystals.

R_F (EtOAc/hexane = 1:7): 0.31

M.p. 170-171 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.23, 1.37 (s, 1 8H, 18/20-H), 6.09 (d, 1 H, $^3J_{15\text{-H, }14\text{-H}}$ = 11.8 Hz, 15-H), 6.17 (dd, 1 H, $^3J_{13\text{-H, }14\text{-H}}$ = 14.2 Hz, $^3J_{13\text{-H, }12\text{-H}}$ = 11.2 Hz, 14-H), 6.27 - 6.78 (m, 9 H, 3/5/6/7/8/9/10/11/12-H), 6.91- 6.98 (m, 2 H, 4/14-H), 7.41 (d, 1 H, $^3J_{2\text{-H, }3\text{-H}}$ = 11.9 Hz, 2-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 159.75 (s, C-16), 158.87 (d, C-2), 150.01 (d, C-4), 145.18 (d, C-6), 140.89 (d, C-14), 138.41, 137.16, 135.01, 132.01, 131.82, 131.66, 131.49, 130.28 (d, C-3/5/7/9/10/11/12/13), 125.37 (d, C-13), 123.97 (d, C-15), 114.19, 112.19 (s, C-a/b), 79.95 (s, C-1), 39.12, 38.06 (s, C-17/19), 33.79, 31.68 (q, C-18/20).

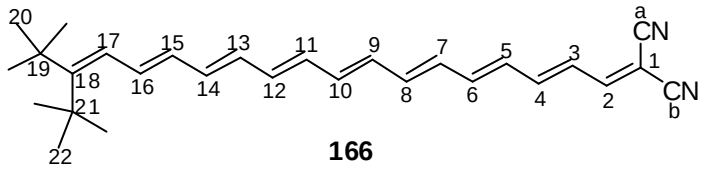
IR (KBr): $\tilde{n}$ = 2953 cm^{-1} (CH, w), 2218 (C≡N, m), 1514 (C=C, s), 1215 (w), 1133 (s), 1007(s).

MS (70 eV): *m/z* (%) = 374 [M^++2] (8), 373 [M^++1] (16), 372 [M^+] (54), 317 (12), 316 (28), 315 [M^+- $C(CH_3)_3$] (100), 288 (26), 157 (20), 155 (40), 146 (41), 115 (22), 95 (22), 94 (45), 91 (44), 79 (33), 66 (20), 57 [$C(CH_3)_3$] (52).

UV ($CHCl_3$): λ_{max} (lg ε) = 274 nm (3.96), 324 (4.35), 536 (4.83).

Due to the very small quantity of the substance no elemental analysis could be obtained.

4.3.32: 2-(17-*tert*-Butyl-18,18-dimethyl-nonadeca-2,4,6,8,10,12,14,16-octaenylidne)-malononitrile (166)



166

A mixture of 30 mg (0.087 mmol) of the aldehyde **47g**, 6 mg (0.087mmol) of malononitrile and 0.1 mg (0.0011 mmol) of β-alanine was stirred for 3.5 h in refluxing 95% EtOH (10 mL) under N_2. When the reaction was cooled to room temp. a black, sticky material formed. It was dissolved in Et_2O and the solution was diluted with water. After the separation of phases the aqueous phase was extracted several times with Et_2O. The combined organic phases were dried with anhydrous $MgSO_4$, the solvent was evaporated and residue was recrystallized from hexane: 25 mg (0.062 mmol, 73%) of the desired compound as black crystals. The same reaction was also carried out with the same amount of starting materials but in toluene (10 mL). After 3.5 h reflux the reaction yielded **166** in 90% (30 mg, 0.077 mmol).

R_F (EtOAc/hexane = 1:7): 0.28.

M.p. 170-171 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.23, 1.37 (s, 18 H, 20/22-H), 6.09 (d, 1 H, $^3J_{17\text{-H, }16\text{-H}}$ = 11.7 Hz, 17-H), 6.16 (dd, 1 H, $^3J_{15\text{-H, }16\text{-H}}$ = 14.3 Hz, $^3J_{15\text{-H, }14\text{-H}}$ = 11.1 Hz, 15-H), 6.26 - 6.78 (m, 1 H, 3/5/6/7/8/9/10/11/12/13/14-H), 6.88 - 6.98 (m, 2 H, 4/16-H), 7.41 (d, 1 H, $^3J_{2\text{-H, }3\text{-H}}$ = 11.9 Hz, 2-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 159.19 (s, C-18), 158.85 (d, C-2), 149.98 (d, C-4), 145.15 (d, C-6), 140.83 (d, C-16), 138.37, 136.77, 136.12, 134.37, 132.18, 132.13, 132.07, 131.87, 131.67, 130.37, 125.41 (d, C-3/5/7/8/9/10/11/12/13/14/15), 123.99 (d, C-17), 114.20, 112.20 (s, C-a/b), 79.94 (s, C-1), 39.08, 38.02 (s, C-19/21), 33.78, 31.70 (q, C-20/22).

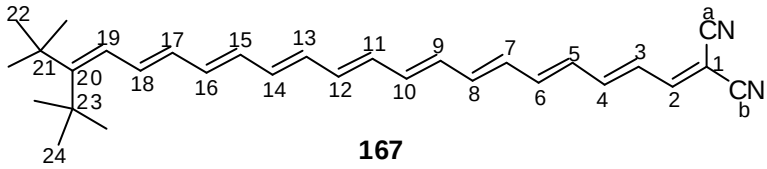
IR (KBr): $\tilde{n}$ = 2958 cm^{-1} (CH, m), 2223 (C≡N, m), 1684 (w), 1593 (m), 1560 (m), 1506 (C=C, s), 1366 (w), 1190 (m), 1163 (m), 1128 (s), 1007 (s).

MS (70 eV): *m/z* (%) = 400 [M^++2] (4), 399 [M^++1] (20), 398 [M^+] (70), 372 [M^+-CN] (3), 342 (22), 341 [M^+- $C(CH_3)_3$] (90), 315 (12), 314 (32), 221 (10), 195 (40), 157 (18), 143 (26), 129 (30), 115 (33), 91 (39), 77 (20), 57 [$C(CH_3)_3$] (100).

UV ($CHCl_3$): λ_{max} (lg ε) = 290 nm (4.09), 344 (4.31), 372 (4.21), 402 (4.22), 534 (4.53).

Due to the very small quantity of the substance no elemental analysis could be obtained.

4.3.33: 2-(19-*tert*-Butyl-20,20-dimethyl-henicosa-2,4,6,8,10,12,14,16,18-nonaenylidene)-malononitrile (167)



167

A mixture of 68 mg (0.181 mmol) of the aldehyde **47h**, 12 mg (0.181mmol) of malononitrile and 0.1 mg (0.0011 mmol) of β-alanine was stirred for 4 h in refluxing toluene (10 mL) under N_2. When the reaction was cooled to room temp. a black, sticky material formed. It was dissolved in Et_2O and the solution was diluted with water. After separation of the phases the aqueous phase was extracted with Et_2O several times. The combined organic phases were dried with anhydrous $MgSO_4$, the solvent was evaporated and the residue was purified by column chromatography on silica gel using CH_2Cl_2/ hexane = 10:1 (v/v): 30 mg (0.72 mmol, 40%) **167** was obtained as a black solid.

R_F (EtOAc/hexane = 1:7): 0.27.

R_F (CH_2Cl_2/hexane = 1:7): 0.81.

M.p. 176-178 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.16, 1.30 (s, 1 8H, 22/24-H), 6.01 (d, 1 H, $^3J_{19\text{-H, }18\text{-H}}$ = 11.7 Hz, 19-H), 6.12 (dd, 1 H, $^3J_{17\text{-H, }18\text{-H}}$ = 14.4 Hz, $^3J_{17\text{-H, }16\text{-H}}$ = 11.7 Hz, 18-H), 6.27 - 6.69 (m, 1 3H, 3/5/6/7/8/9/10/11/12/13/14/15/16-H), 6.82 (m, 2 H, 4/18-H), 7.35 (d, 1 H, $^3J_{2\text{-H, }3\text{-H}}$ = 12.0 Hz, 2-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 158.82 (d, C-2), 149.94 (d, C-4), 145.10 (d, C-6), 140.79 (d, C-18), 138.32, 136.73, 135.74, 135.44, 133.95, 132.43, 132.20, 132.01, 131.75, 130.41, 125.44 (d, C-3/5/7/8/9/10/11/12/13/14/15/16/17), 123.99 (d, C-19), 114.58, 112.29 (s, C-a/b), 80.00 (s, C-1), 39.05, 37.99 (s, C-21/23), 33.76, 31.71 (q, C-22/24).

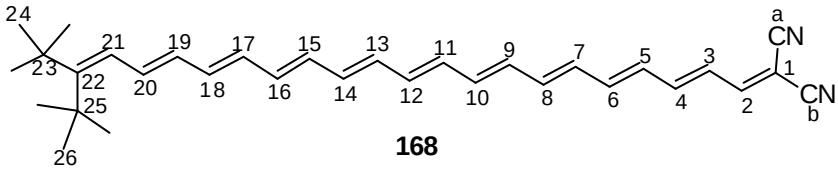
IR (KBr): $\tilde{n}$ = 2961 cm^{-1} (CH, m), 2223 (C≡N, m), 1577 (m), 1503 (C=C, s), 1262 (w), 1156 (w), 1124 (s), 1010 (s).

MS (70 eV): *m/z* (%) = 424 [M^+] (16), 367 [M^+- $C(CH_3)_3$] (22), 340 (8), 235 (6), 221 (10), 143 (11), 128 (14), 115 (16), 105 (12), 91 (16), 77 (12), 57 [$C(CH_3)_3$] (100).

UV ($CHCl_3$): λ_{max} (lg ε) = 304 nm (4.14), 362 (4.47), 556 (4.87).

Due to the very small quantity of the substance no elemental analysis could be obtained.

4.3.34: 2-(21-*tert*-Butyl-22,22-dimethyl-tricosa-2,4,6,8,10,12,14,16,18,20-decaenylidene)-malononitrile (168)



168

A mixture of 30 mg (0.074 mmol) of **47i**, 10 mg (0.074mmol) of malononitrile and 0.1 mg (0.0011 mmol) of β-alanine was stirred for 6 h in refluxing toluene (10 mL) under N_2. When the reaction was cooled to room temp. a black, sticky material formed. It was dissolved in Et_2O and the solution was diluted with water. After separation of the phases the aqueous phase was extracted with Et_2O several times. The combined organic phases were dried with anhydrous $MgSO_4$, the solvent was evaporated and the residue was

purified by column chromatography on silica gel using CH_2Cl_2 as the eluent: 10 mg (0.022 mmol, 30%) **167** was obtained as a black solid.

R_F (EtOAc/hexane = 1:7): 0.27.

R_F (CH_2Cl_2): 0.78.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.15, 1.30 (s, 18 H, 24/26-H), 6.02-6.91 (m, 19 H, 3/4/5/6/7/8/9/10/11/12/13/14/15/16/17/18/19/20/21-H), 7.34 (d, 1 H, $^3J_{2\text{-H, }3\text{-H}}$ = 11.8 Hz, 2-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 158.83 (d, 2-C), 149.96 (d, C-4), 145.12 (d, C-6), 140.80 (d, C-20), 138.33, 136.74, 135.75, 135.46, 133.96, 132.45, 132.40, 132.26, 132.21, 132.11, 132.01, 131.77, 130.43, 125.44 (d, C-4/6/8/9/10/11/12/13/14/15/16/17/18/19/20/21/22), 124.00 (d, C-21), 114.21, 112.21 (s, a/b-C), 79.95 (s, C-1), 39.06, 37.99 (s, 23/25-C), 33.76, 31.72 (q, C-24/26).

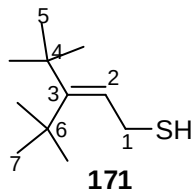
IR (KBr): $\tilde{n}$ = 2960 cm^{-1} (CH, m), 2224 (C≡N, m), 1725 (m), 1684 (m), 1578 (m), 1559 (m), 1503 (C=C, s), 1467 (w), 1217 (m), 1164 (s), 1124 (s), 1008 (s).

MS (70 eV): *m*/*z* (%) = 452 [M^++2] (0.4), 451 [M^++1] (1.2), 450 [M^+] (3.5), 425 (30), 424 [M^+-CN] (90), 393 [M^+- $C(CH_3)_3$] (5), 368 (34), 367 (100), 340 (24), 221 (24), 198 (14), 165 (14), 143 (22), 129 (24), 115 (22), 91 (32), 79 (15), 57 [$C(CH_3)_3$] (84).

UV ($CHCl_3$): λ_{max} (lg ε) = 306 nm (4.18), 363 (4.50), 556 (4.85).

Due to the very small quantity of the substance no elemental analysis could be obtained.

4.3.35: 3-*tert*-Butyl-4,4-dimethyl-pent-2-ene-1-thiol (171)



171

A stirred mixture of 0.250 g (1.32 mmol) of **129** and 0.100 g (1.32 mmol) of thiourea in 7 mL of anhydrous ethanol was refluxed for 3 h under N_2. During reflux formation of a white solid was observed. After the reaction was cooled to room temp. the solid was dissolved by addition of aqueous KOH solution (30 mg, 7.5 mmol KOH in 1.4 mL H_2O).

The mixture was acidified (pH ≅ 5) with 2M HCl and again a white precipitate formed. The precipitate was filtered through a Büchner funnel and washed first with H_2O, then several times with ether. The filtrates were combined and the phases were separated. The aqueous phase was extracted several times with ether. The combined organic phases were dried with $MgSO_4$ and the solvent was evaporated. Purification of the residue by column chromatography on silica gel using ethylacetate/hexane = 1:2 (v/v) yielded 0.219 g (1.18 mmol, 90%) thiol **171** as a colourless oil.

R_F (ethylacetate/hexane = 1:2): 0.65.

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.11, 1.23 (s, 18 H, 5/7-H), 1.37 (t, 1 H, $^3J_{SH,\ 2\text{-}H}$ = 7.1 Hz, SH), 3.40 (q, 2 H, $^3J_{1\text{-}H,\ 2\text{-}H}$ = 8.1 Hz and $^3J_{1\text{-}H,\ SH}$ = 7.1 Hz, 1-H), 5.33 (t, 1 H, $^3J_{2\text{-}H,\ 1\text{-}H}$ = 8.1 Hz, 2-H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 154.33 (s, C-3), 124.15 (d, C-2), 38.53, 37.15 (s, C-4/6), 33.27, 31.77 (q, C-5/7), 25.53 (t, C-1).

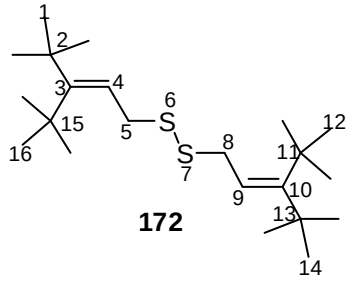
IR (KBr): $\tilde{n}$ = 2958 cm^{-1} (vs), 2919 (s), 2873 (m), 1484 (m), 1391 (m), 1378 (m), 1366 (m), 1244 (m), 1218 (m), 1085 (w), 859 (w), 685 (m).

MS (GC-MS): *m/z* (%) = 186 [M^+] (10), 171, 152, 139 (10), 129 [M^+-$C(CH_3)_3$] (15), 117 (10), 112, 95 (50), 84 (25), 75, 69 (30), 57 [$C(CH_3)_3$] (100).

UV (CH_3CN): λ_{max} (lg ε) = 198 nm (4.04), 224 (3.35), 228 (3.14), 236 (2.84).

HRMS $C_{11}H_{22}S$ (186.4) Calc. 186.1442
Found 186.1432 ± 2 ppm

4.3.36: 3-*tert*-Butyl-1-(3-*tert*-butyl-4,4-dimethyl-pent-2-enyldisulfanyl)-4,4-dimethyl-pent-2-ene (172)



172

To a cold solution (10 °C) of 258 mg (6.45 mmol) NaOH in 1.17 mL of water was added 200 mg (1.075 mmol) of thiol **171**. A white solid formed immediately. The reaction mixture was stirred for 10 min followed by addition of 0.075 mL of 30% H_2O_2. After 10 min of stirring glacial acetic acid was added (pH ≅ 5) and the mixture extracted several times with ether. The combined organic phases were neutralized with aqueous K_2CO_3 solution. The phases were separated, the organic phase was dried with $MgSO_4$ and the solvent was evaporated. The reaction yielded 190 mg (0.513 mmol, 96 %) disulfide **172** as a colorless low melting (~10°C) solid.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.12, 1.24 (s, 36 H, 1/12/14/16-H), 3.64 (d, 4 H, $^3J_{5\text{-H, 4-H and 8-H, 9-H}}$ = 8.2 Hz, 5/8-H), 5.38 (t, 2 H, $^3J_{4\text{-H, 5-H and 9-H, 8-H}}$ = 8.2 Hz, 4/9-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 157.38 (s, C-3/10), 119.80 (d, C-4/9), 41.32 (t, C-5/8), 38.97, 37.29 (s, C-2/11/13/15).

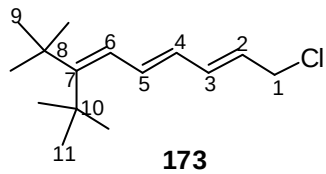
IR (KBr): $\tilde{n}$ = 2958 cm^{-1} (vs), 2918 (s), 2873 (m), 1608 (w), 1484 (m), 1470 (m), 1402 (m), 1390 (m), 1366 (m), 1241 (m), 1218 (m), 1078 (m), 972 (w), 865 (w).

MS (70 eV): *m*/*z* (%) = 370 [M^+] (2), 190 (2), 178 (9), 153 (9), 141 (5), 122 (9), 111 (7), 97 (35), 83 (14), 69 (20), 57 [$C(CH_3)_3$] (100).

UV (CH_3CN): λ_{max} (lg ε) = 194 nm (4.40), 200 (4.39), 204 (4.37), 212 (4.34, sh), 216 (4.32), 244 (3.44), 262 (3.10).

Although all the spectroscopic data are consistent with the proposed structure, elemental analysis of this substance did not yield satisfactory elemental composition.

4.3.37: 7-*tert*-Butyl-1-chloro-8,8-dimethyl-nona-2,4,6-triene (173)



173

To a stirred mixture of 0.800 g (3.60 mmol) of crude **149a** (see Exp. 4.3.17) and 0.360 g (4.5 mmol) of pyridine in anhydrous ether (5 mL) at 0 °C was added dropwise 1.07 g (9.00 mmol) of $SOCl_2$ in ether (5 mL) under N_2. The reaction was allowed to reach room

temp. then stirred for an additional 2 h. The mixture was hydrolyzed, then extracted several times with ether. The combined organic phases were dried with $MgSO_4$ and the solvent was evaporated. The compound **173** was found to be highly unstable and it polymerized readily. Besides, chromatographic purification was observed to cause solvolysis of the highly reactive chloride to the alcohol **149a**. The compound could hence not be purified, but was used as a crude mixture for the subsequent reaction (Exp. 4.3.38): 430 mg (50%).

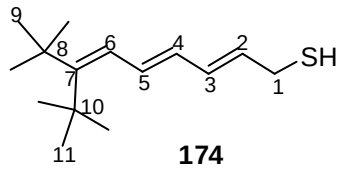
R_F (EtOAc/hexane = 2:10): 0.40.

^{1}H NMR (100.1 MHz, $CDCl_3$): δ = 1.05, 1.20 (s, 18 H, 9/11-H), 3.97 (d, 2 H, $^3J_{1\text{-H, }2\text{-H}}$ = 7.4 Hz, 1-H), 5.52 - 5.67 (m, 1 H, 2-H), 5.84 - 5.96 (m, 2 H, 4/6-H), 6.17 - 6.30 (dd, 1 H, $^3J_{5\text{-H, }4\text{-H}}$ = 15.6 Hz and $^3J_{5\text{-H, }6\text{-H}}$ = 10.9 Hz, 5-H), 6.65 - 6.78 (dd, 1 H, $^3J_{3\text{-H, }2\text{-H}}$ = 14.6 Hz and $^3J_{3\text{-H, }4\text{-H}}$ = 11.7 Hz, 3-H).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 149.2 (s, C-7), 135.17, 133.68, 130.51, 125.18, 123.39 (d, C-2/3/4/5/6), 69.40 (t, C-1), 39.20, 38.60 (s, C-8/10), 33.73, 31.72 (q, C-9/11).

MS (70 eV): *m*/*z* (%) = 240 [M^+] (14), 205 [M^+-Cl] (6), 183 [M^+-$C(CH_3)_3$] (42), 155 (9), 147 (28), 133 (18), 119 (17), 105 (24), 91 (30), 81 (12), 79 (16), 57 [$C(CH_3)_3$] (100), 43 (10).

4.3.38: 7-*tert*-Butyl-8,8-dimethyl-nona-2,4,6-triene-1-thiol (174)



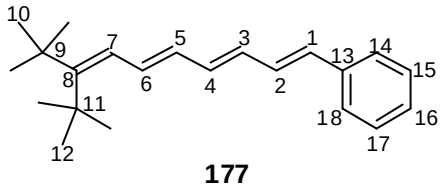
174

A mixture of 0.400 g of crude **173** (see Exp. 9.3) and 0.127 g (1.66 mmol) of thiourea in anhydrous ethanol (10 mL) was refluxed for 3 h under N_2. After cooling to room temp. a solution of 0.59 g (0.95 mol) KOH in 2.80 mL of water was added and the formation of a white solid was observed. The solid was dissolved by addition of 2M H_2SO_4 (pH ≅ 3). After separation of the phases the aqueous phase was extracted several times with ether. The combined organic phases were dried with $MgSO_4$ and the solvent was evaporated in a rotary evaporator.

The ^{1}H NMR spectra of the crude mixture showed the presence of thiol **174**, however the compound was highly unstable and could not be purified or characterized fully.

^{1}H NMR (100.1 MHz, $CDCl_3$): δ = 1.21, 1.36 (s, 18 H, 9/11-H), 1.36 (t, 1 H, SH), 3.24 (t, 2 H, 1-H), 5.68-5.82 (m, 1 H, 2-H), 5.99-6.31 (m, 3 H, 3/4/6-H), 6.72-6.85 (dd, 1 H, $^{3}J_{5\text{-H, }4\text{-H}}$ = 14.3 Hz and $^{3}J_{5\text{-H, }6\text{-H}}$ = 11.6 Hz, 5-H).

4.3.39: (8-*tert*-Butyl-9,9-dimethyl-deca-1,3,5,7-tetraenyl)-benzene (177)



177

To a stirred suspension of 0.441 g (1.13 mmol) of **176** in anhydrous THF (10 mL) was added 0.121 g (1.08 mml) of *t*-BuOK. After 30 min 0.1 g (0.454 mmol) of **47b** in THF (5 mL) was added and the reaction mixture was stirred for 3 h. The mixture was diluted with water and extracted several times with ether. The combined organic phases were dried with $MgSO_4$ and after solvent evaporation the remaining residue was purified by column chromatography on silica gel using ethylacetate/hexane = 1:10 (v/v) as the eluent. After chromatography 0.20 g (0.7 mmol, 70%) of **177** was obtained as an *E*/*Z* mixture. Also 12 mg (0.07 mmol, 7%) of stilbene (**178**) was formed as a side product. Sublimation of the isomer mixture at 80 °C/ 8 mbar gave only the *E*-isomer (0.120 g, 41%) as a yellow solid. A black residue remained in the sublimation flask assumed to be formed by decomposition/polymerization of *Z*-**177**.

R_F (ethylacetate/hexane = 1:10): 0.90.

M.p. 80-82 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.16, 1.31 (s, 18 H, 10/12-H), 6.02 (d, 1 H, $^{3}J_{7\text{-H, }6\text{-H}}$ = 11.7 Hz, 7-H), 6.10 (dd, 1 H, $^{3}J_{5\text{-H, }6\text{-H}}$ = 14.4 Hz and $^{3}J_{5\text{-H, }4\text{-H}}$ = 10.6 Hz, 5-H), 6.30 (dd, 1 H, $^{3}J_{3\text{-H, }4\text{-H}}$ = 14.8 Hz and $^{3}J_{3\text{-H, }2\text{-H}}$ = 10.4 Hz, 3-H), 6.40 (dd, 1 H, $^{3}J_{4\text{-H, }3\text{-H}}$ = 14.8 Hz and $^{3}J_{4\text{-H, }5\text{-H}}$ = 10.6 Hz, 4-H), 6.46 (d, 1 H, $^{3}J_{1\text{-H, }2\text{-H}}$ = 15.5 Hz, 1-H), 6.79 (m, 2 H, 2/6-H), 7.12 (m, 1 H, 16-H), 7.23 (m, 2 H, 15/17-H), 7.31 (d, 2 H, ^{3}J = 8.0 Hz, 14/18-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 157.92 (s, C-8), 137.55 (s, C-13), 134. 17 (d, C-4), 133.09 (d. C-6), 132.19, 132.17 (d, C-5/3), 131.82 (d, C-1), 129.37 (d, C-2), 128.60 (d, C-15/17), 127.31 (d, C-16), 126.24 (d, C-14/18), 123.98 (d, C-7), 39.01, 37.95 (s, C-9/11), 33.79, 31.80 (q, C-10/12).

IR (KBr): $\tilde{n}$ = 3012 cm^{-1} (Ar, m), 3003 (m), 2957 (s), 2923 (m), 2871 (m), 1725 (m), 1698 (w), 1686 (w), 1602 (w), 1582 (C=C, w), 1482 (m), 1389 (m), 1217 (m), 1002 (vs), 746 (m), 691 (m).

MS (70 eV): *m/z* (%) = 295 [M^++1] (18), 294 [M^+] (85), 237 [M^+- $C(CH_3)_3$] (100), 210 (18), 195 (18), 181 (13), 179 (7), 165 (5), 131 (4), 117 (5), 105 (4), 91 (5), 57 [$C(CH_3)_3$] (2).

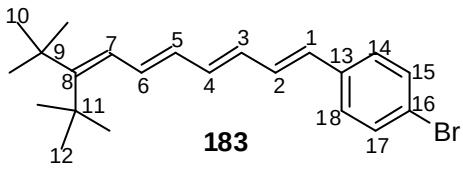
UV ($CHCl_3$): λ_{max} (lg ε) = 254 nm (3.79), 306 (4.03), 316 (4.23), 324 (4.33), 336 (4.54), 352 (4.69), 370 (4.60).

HRMS $C_{22}H_{30}$ (294.5) Calc. 294.2340

Found 294.2347 ± 2 ppm

The spectral data of stilbene (**178**) are in accordance with the data given in literature[82].

4.3.40: 1-Bromo-4-(8-*tert*-butyl-9,9-dimethyl-deca-1,3,5,7-tetraenyl)-benzene (183)



183

To a stirred suspension of 0.220 g (1.0 mmol) of **47b** and 1.280 g (2.5 mmol) of *p*-bromobenzyltriphenylphosphoniumbromide **182** in anhydrous THF (15mL) was added 0.270 mg (2.4 mmol) of *t*-BuOK. The colour of the reaction first turned to dark orange, then to yellow. After reflux for 2 h the reaction mixture was hydrolyzed and extracted several times with ether. The combined organic phases were dried with $MgSO_4$ and the solvent was evaporated. Chromatographic purification on silica gel using ethylacetate: hexane = 1/10 (v/v) as the eluent yielded 80 mg (0.215 mmol, 21%) **183** as yellow solid. From the reaction 202 mg (0.600 mmol, 60%) di-bromostilbene (**184**) was also obtained.

R_F (ethylacetate: hexane = 1/10): 0.90.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.16, 1.31 (s, 18 H, 10/12-H), 6.01 (d, 1 H, $^3J_{7\text{-H, }6\text{-H}}$ = 11.7 Hz, 7-H), 6.10 (dd, 1 H, $^3J_{5\text{-H, }6\text{-H}}$ = 14.3 Hz and $^3J_{5\text{-H, }4\text{-H}}$ = 10.9 Hz, 5-H), 6.28 (dd, 1 H, $^3J_{3\text{-H, }4\text{-H}}$ = 14.7 Hz and $^3J_{3\text{-H, }2\text{-H}}$ = 10.6 Hz, 3-H), 6.36 - 6.44 (m, 2 H, H-1/4-H), 6.75 (dd, 1 H, $^3J_{2\text{-H, }1\text{-H}}$ = 15.5 Hz and $^3J_{2\text{-H, }3\text{-H}}$ = 10.6 Hz, 2-H), 6.83 (dd, 1 H, $^3J_{6\text{-H, }5\text{-H}}$ = 14.2 Hz and $^3J_{6\text{-H, }7\text{-H}}$ = 11.8 Hz, 6-H), 7.17 (d, 2 H, $^3J_{14\text{-H, }15\text{-H and }18\text{-H, }17\text{-H}}$ = 8.5 Hz, 14/18-H), 7.34 (d, 2 H, $^3J_{15\text{-H, }14\text{-H and }17\text{-H, }18\text{-H}}$ = 8.5 Hz, 15/17-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 180.77 (s, C-16), 158.32 (s, C-9), 136.50 (s, C-13), 134.88 (d, C-1), 133.58 (d, C-6), 132.09 (d, C-5), 131. 80, 131.76 (d, C-3/15/17-C), 130.43 (d, C-4), 130.10 (d, C-2), 127.70 (d, 14/18-C), 123.98 (d, C-7), 39.36, 38.29 (s, C-9/11), 34.10, 32.09 (q, C-10/12).

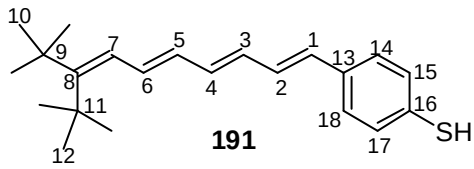
IR (KBr): $\tilde{n}$ = 3029 cm^{-1} (Ar, w), 3015 (w), 2959 (m), 2956 (m), 2925 (m), 1636 (w), 1485 (m), 1365 (w), 1261 (m), 1072 (m), 1057 (m), 1008 (m), 993 (s), 824 (m), 802 (m), 795 (m).

MS (70 eV): *m/z* (%) = 372 [M^+] (42), 317 [M^+-$C(CH_3)_3$] (100), 288 (16), 236 (12), 221 (14), 207 (10), 194 (12), 179 (10), 169 (22), 146 (15), 130 (20), 116 (42), 57 [$C(CH_3)_3$] (32), 41 (14).

UV ($CHCl_3$): λ_{max} (lg ε) = 230 nm (3.86), 240 (3.80), 260 (3.76), 268 (3.80), 314 (4.27), 324 (4.38), 340 (4.53), 358 (4.65), 376 (4.57).

Although all the spectroscopic data are consistent with the proposed structure, elemental analysis of this substance did not yield satisfactory elemental composition.

4.3.41: 4-(8-*tert*-butyl-9,9-dimethyl-deca-1,3,5,7-tetraenyl)-benzenethiol (191)



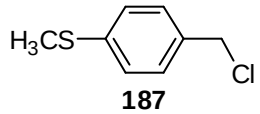
191

0.220 mL of *n*-BuLi (1.6 M in hexane) was added to a stirred solution of 60 mg (0.160 mmol) of **183** in anhydrous ether (5 mL) at room temp under N_2. The reaction was stirred for 1.5 h. The colour of the reaction mixture first turned to reddish brown and at the end it was light orange. Then 11 mg (0.350 mmol) of sulfur was added and stirring was

continued for 20 h. The reaction mixture was cooled to 0 °C and hydrolyzed with 5 mL of water. After separation of the phases the organic phase was washed with 5 mL of water, dried with $MgSO_4$, and the solvent was evaporated. The remaining residue was diluted with anhydrous ether (4 mL) and was added dropwise to a suspension of 0.011 g (0.305 mmol) of $LiAlH_4$ in ether (2 mL). The reaction was refluxed for 2 h, then cooled to 0 °C and 1 mL of HCl (6N) was added. The phases were separated and the aqueous phase was extracted with ether, dried with $MgSO_4$ and the solvent was evaporated. The ^{1}H NMR spectrum of the residue showed the presence of a compound which was assigned structure **204**. However, no purification or further characterization were possible, the compound polymerized quickly.

^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.14 (s), 1.31 (s), 5.91 – 7.30 (m), 7.43 (d, ^3J = 8.1 Hz).

4.3.42: 4-(Mercaptomethyl)-benzylchloride (187)

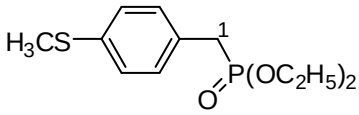


187

To a stirred solution of 5 g (32 mmol) of 4-(mercaptomethyl)-benzylchloride in anhydrous toluene (15 mL) was dropwise added 2.6 mL (36 mmol) of $SOCl_2$ under N_2. During the addition the colour of the reaction changed from colourless to green, then to yellow. The reaction mixture was heated upto 80 °C and stirred for 2 h. After cooling to room temp. excess $SOCl_2$ and the solvent were removed in vacuo. From the distillation of the remaining brown residue 5.41 g (31 mmol, 97%) of **187** was obtained at 105°C/ 0.5 mbar as a colourless liquid.

The spectral data of compound **187** are in accordance with the data given in literature.[71]

4.3.43: 4-(Mercaptomethyl)-benzyl-diethylphosphonate (188)

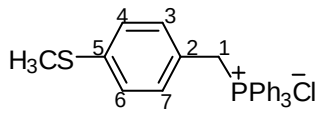


188

A stirred mixture of 4 g (23 mmol) of **187** and 4.23 g (25 mmol) of triethylphosphite was refluxed (160 °C) for 3 h. After the reaction mixture had been cooled to room temp. the product was purified by vacuum distillation at 154 °C/ 2 mbar: 5.12 g (18 mmol, 89%; Lit. 89%[71]) of **188** was obtained as colourless oil.
In ref.[71] only the ^{1}H NMR data of **188** are given.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.28 (t, 6 H, CH_3), 2.49 (s, 3 H, S-CH_3), 3.10 - 3-15 (d, 2 H, ^3J = 21.6 Hz, H-1), 4.02-4.06 (m, 4 H, O-CH_2), 7.24 (s, 4 H, Ar).
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 136.90, 136.86 (s), 130.26, 130.19 (d), 129.04, 128.40, 128.31 (s), 126.80, 126.77 (d), 62.11, 62.05 (t, C-1), 33.89, 32.48 (t, O-CH_2), 16.36, 16.30 (q), 15.87 (q, S-CH_3).
IR (KBr): $\tilde{n}$ = 2982 cm^{-1} (m), 2921 (m), 2908 (m), 1653 (w), 1648 (w), 1495 (m), 1440 (m), 1407 (m), 1392 (m), 1247 (s), 1190 (m), 1163 (m), 1096 (m), 1054 (vs), 1027 (vs), 965 (vs), 852 (m), 772 (m), 647 (m).
MS (70 eV): *m/z* (%) = 275 [M^++1] (8), 274 [M^+] (63), 246 (6), 137 [M^+- $PO(OC_2H_5)_2$] or [M^+- CH_3SPhCH_2] (100), 122 (13), 91 (5).

4.3.44: 4-(Mercaptomethyl)-benzyl-triphenylphosphonium chloride (189)



189

A stirred mixture of 1.91 g (11 mmol) of **187** and 2.90 g (11 mmol) of triphenylphosphine in acetone (10 mL) was refuxed for 3 h under N_2. With the start of the reflux a white precipitate began to form. The reaction was stirred overnight at room temp. The white solid **189** was filtered through a Büchner funnel, washed several times with acetone and dried under high vacuum: 1.91 g (4.4 mmol, 40%) of **189**, white solid.

M.p. 196-198 °C.
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, S-CH_3), 4.48 (d, 2 H, ^3J = 14.4 Hz, H-1), 6.94 - 7.05 (m, 4 H, 3/4/6/7-H), 7.59 - 7.64 (m, 6 H, Ph), 7.73 - 7.78 (m, 9 H, Ph).

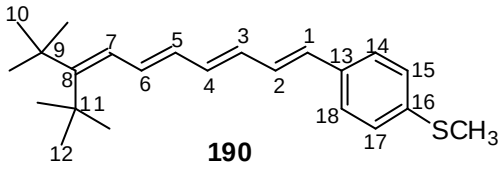
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 139.03(s), 138.99 (s), 134.91 (d), 134.88 (d), 134.52 (d), 134.42 (d), 132.02 (d), 131.97 (d), 130.20 (d), 130.07 (d), 126.27 (d), 126.24 (d), 118.35 (s), 117.51 (s), 30.37, 29.81 (t, C-1), 15.31 (q, S-CH_3).

IR (KBr): $\tilde{n}$ = 3655 cm^{-1} (w), 3313 (w), 3037 (w), 2987 (w), 2777(m), 1622 (w), 1587 (w), 1494 (m), 1438 (vs), 1426 (m), 1405 (m), 1335 (w), 1313 (w), 1201 (w), 1187 (w), 1163 (w), 1111 (vs), 1094 (m), 997 (m), 841 (m), 832 (m), 749 (s), 719 (s), 691 (s), 684 (s), 645 (m), 537 (vs), 509 (vs), 503 (vs).

MS (FAB positive): *m*/*z* (%) = 400 [M^+-Cl] (31), 399 (100), 262 [PPh_3] (14), 183 (14), 154 (34), 137 [CH_3SPhCH_2] (100), 107 (14), 77 [C_6H_5] (20), 63 (8).

UV ($CHCl_3$): λ_{max} (lg ε) = 196 nm (5.10), 228 (4.48), 232 (4.41), 268 (4.27), 280 (4.12), 290 (3.87).

4.3.45: 1-(8-*tert*-Butyl-9,9-dimethyl-deca-1,3,5,7-tetraenyl)-4-methylsulfanyl-benzene (190)



190

4.3.45.a: Synthesis of 190 using phosphonate 188

To a solution of 0.202 g (2 mmol) of diisopropylamine in anhydrous THF (10 mL) at −78 °C was added dropwise 1.25 mL of *n*-BuLi (1.6 M in hexane) under N_2, and the reaction mixture was stirred for 10 min. A solution of 0.548 g (2 mmol) **188** in THF (5mL) was added and stirring was continued for 30 more min, 0.400 g (1.82 mol) **47b** in THF (5mL) was added and the mixture was left to warm up to room temp. The reaction mixture was hydrolyzed with aqueous NH_4Cl solution, the phases were separated, and the aqueous phase was extracted several times with ether. The combined organic phases were washed with water, dried with $MgSO_4$, and the solvent was evaporated. The remaining residue was purified by column chromatography on silica gel using ethylacetate: hexane = 1/5 (v/v) as the eluent: 0.124 g (0.364 mmol, 20%) of **190**, yellow solid.

4.3.45.b: Synthesis of 190 using phosphonium salt 189

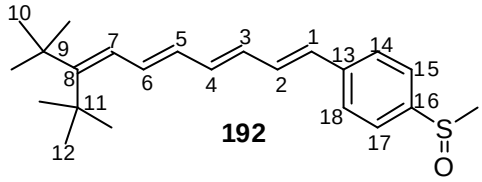
To a suspension of 0.400 g (0.920 mmol) of 189 in anhydrous THF (10 mL) was first added 0.101 g (0.460 mmol) of 47b in THF (5 mL) followed by 98 mg (0.875 mmol) of *t*-BuOK. The colour of the solution turned immediately from white to dark red. The reaction was monitored by TLC using ethylacetate: hexane = 1/5 (v/v) as the eluent, the starting material had been consumed after 5 min. The reaction mixture was hydrolyzed and the phases were separated. The combined organic phases were dried with $MgSO_4$ and the solvent was evaporated in a rotary evaporator. The ^{1}H NMR spectrum of the crude product showed a mixture of isomers in a 1:19 ratio according to the peak intensity. The purification and separation of isomers was performed by column chromatography using ethylacetate/hexane = 1:5 (v/v). The all-*trans* isomer 190 was obtained in 61% yield (95 mg, 0.280 mmol). The other product, presumably the *cis*-isomer, could not be characterized because of the very low amount (ca. 5 mg).

R_F (EtOAc/hexane = 1:5) 0.67 (all-*trans* isomer).
M.p. 118-119 °C.
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.23, 1.38 (s, 18 H, 10/12-H), 6.08 (d, 1 H, $^3J_{7\text{-H, 6-H}}$ = 11.7 Hz, 7-H), 6.17 (dd, 1 H, $^3J_{5\text{-H, 6-H}}$ = 14.3 Hz and $^3J_{5\text{-H, 4-H}}$ = 10.6 Hz, 5-H), 6.35 (dd, 1 H, $^3J_{3\text{-H, 4-H}}$ = 14.7 Hz and $^3J_{3\text{-H, 2-H}}$ = 10.3 Hz, 3-H), 6.42-6.50 (m, 2 H, 1/4-H), 6.80 (dd, 1 H, $^3J_{2\text{-H, 1-H}}$ = 15.4 Hz and $^3J_{2\text{-H, 3-H}}$ = 10.4 Hz, 2-H), 6.87 (dd, 1 H, $^3J_{6\text{-H, 5-H}}$ = 14.2 Hz and $^3J_{6\text{-H, 7-H}}$ = 11.7 Hz, 6-H), 7.17 (d, $^3J_{15\text{-H, 14-H and 17-H, 18-H}}$ = 8.4 Hz, 2H, 15/17-H), 7.34 (d, 2 H, $^3J_{14\text{-H, 15-H and 14-H, 18-H}}$ = 8.4 Hz, 14/18-H).
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 196.98 (s, C-16), 157.90 (s, C-8), 137.46 (s, C-13), 134.05 (d, C-1), 133.08 (d, C-6), 132.27, 132.23 (d, C-3/5), 131.23 (C-4), 128.89 (d, C-2), 126.75 (d, C-15/17), 126.66 (d, C-14/18), 124.03 (d, C-7), 39.02, 37.95 (s, C-9/11), 33.83, 31.85 (q, C-10/12), 15.89 (q, S-CH_3).
IR (KBr): $\tilde{n}$ = 3008 cm^{-1} (m), 2957 (s), 2923 (s), 2871 (m), 1635 (w), 1629 (w), 1491 (m), 1365 (w), 1261 (m), 1217 (m), 1091 (m), 1001 (vs), 801 (m).
MS (70 eV): *m*/*z* (%) = 341 [M^++1] (26), 340 [M^+] (100), 284 (14), 283 [M^+-$C(CH_3)_3$] (68), 256 (13), 163 (12), 137 (90), 116 (10), 57 [$C(CH_3)_3$] (14).

UV (CH_3CN): λ_{max} (lg ε) = 240 nm (3.80), 276 (3.83), 284 (3.89), 314 (4.09), 322 (4.22), 338 (4.48, sh), 352 (4.70), 368 (4.84), 388 (4.75).

Although all the spectroscopic data are consistent with the proposed structure, elemental analysis of this substance did not yield satisfactory elemental composition.

4.3.46: 1-(8-*tert*-Butyl-9,9-dimethyl-deca-1,3,5,7-tetraenyl)-4-methylsulfinyl-benzene (192)



192

To a stirred solution of 60 mg (0.176 mmol) of **190** in CH_2Cl_2 (5 mL) was added 30 mg (0.176 mmol) of mCPBA at 0 °C under N_2. Monitoring the reaction with TLC using ethylacetate as the solvent showed that the conversion of **190** to **192** occurred immediately. 1 mL of HCl (1N) was added and the phases were separated. The aqueous phase was extracted with CH_2Cl_2, dried with $MgSO_4$, and the solvent was evaporated. The purification of the compound was carried out by flash column chromatography on silica gel using ethylacetate under N_2. The reaction yielded 62 mg (0.176 mmol, 100%) of **192** as a yellow solid. The sulfoxide was very unstable towards air oxygen and was converted to the sulfone **193** easily.

R_F (EtOAc): 0.51.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.17, 1.32 (s, 1 8 H, 10/12-H), 2.65 (s, 3 H, S-CH_3), 6.03 (d, 1 H, $^3J_{7\text{-H, }6\text{-H}}$ = 11.7 Hz, 7-H), 6.08 - 6.14 (dd, 1 H, $^3J_{5\text{-H, }6\text{-H}}$ = 14.3 Hz and $^3J_{5\text{-H, }4\text{-H}}$ = 10.9 Hz, 5-H), 6.27 - 6.34 (dd, 1 H, $^3J_{3\text{-H, }4\text{-H}}$ = 14.8 Hz and $^3J_{3\text{-H, }2\text{-H}}$ = 10.7 Hz, 3-H), 6.42 - 6.49 (m, 2 H, 1/4-H), 6.81 - 6.88 (m, 2 H, 2/6-H), 7.44 (d, 2 H, $^3J_{14\text{-H, }15\text{-H and }18\text{-H, }17\text{-H}}$ = 8.4 Hz, 14/18-H), 7.50 (d, 2 H, $^3J_{15\text{-H, }14\text{-H and }17\text{-H, }18\text{-H}}$ = 8.3 Hz, 15/17-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 158.78 (s, C-8), 143.83 (s, C-13), 140.60 (s, C-16), 135.81 (d, C-1), 134.13 (d, C-6), 131.93 (d, C-5), 131.64, 131.53 (d, C-2/3), 130.08 (d, C-

4), 126.95 (d, C-14/18), 123.99, 123.94 (d, C-7/15/17), 43.95 (q, S-CH_3), 39.06, 38.00 (s, C-9/11), 33.80, 31.75 (q, C-10/12).

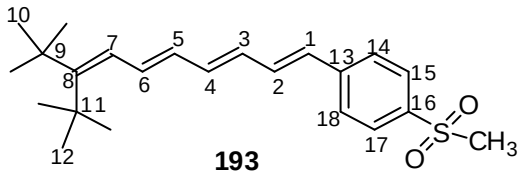
IR (KBr): $\tilde{n}$ = 2994 cm^{-1} (s), 2958 (vs), 2923 (s), 2870 (m), 1700 (m), 1683 (m), 1665 (m), 1637 (m), 1595 (m), 1578 (m), 1483 (m), 1402 (m), 1392 (m), 1366 (m), 1261 (m), 1261 (s), 1087 (vs), 1049 (S=O, vs), 999 (vs), 801 (s).

MS (70 eV): *m/z* (%) = 356 [M^+] (44), 315 (10), 299 [M^+- $C(CH_3)_3$] (100), 284 (46), 272 (8), 255 (14), 193 (12), 179 (16), 167 (28), 151 (16), 137 (23), 116 (21), 107 (9), 91 (9), 57 [$C(CH_3)_3$] (65).

UV (CH_3CN): λ_{max} (lg ε) = 348 nm (4.39), 360 (4.46), 378 (4.36).

Although all the spectroscopic data are consistent with the proposed structure, elemental analysis of this substance did not yield satisfactory elemental composition.

4.3.47: 1-(8-*tert*-Butyl-9,9-dimethyl-deca-1,3,5,7-tetraenyl)-4-methylsulfonyl-benzene (193)



193

To a stirred solution of 30 mg (0.088 mmol) of **190** in CH_2Cl_2 (5 mL) at 0 °C was added 30 mg (0.176 mmol) mCPBA under N_2. Monitoring the reaction by TLC showed that the conversion of **190** to **193** occurred immediately. 1 mL of HCl (1N) was added and the phases were separated. The aqueous phase was extracted with CH_2Cl_2, dried with $MgSO_4$, and the solvent was evaporated. Purification by column chromatography on silica gel using ethylacetate gave 32 mg (0.088 mmol, 100%) of **193** as a yellow solid.

R_F (EtOAc): 0.69.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.17, 1.32 (s, 18H, 10/12-H), 2.97 (s, 3H, S-CH_3), 6.03 (d, 1 H, $^3J_{7\text{-H, }6\text{-H}}$ = 11.7 Hz, 7-H), 6.08 - 6.15 (dd, 1 H, $^3J_{5\text{-H, }6\text{-H}}$ = 14.3 Hz and $^3J_{5\text{-H, }4\text{-H}}$ = 10.9 Hz, 5-H), 6.28 - 6.34 (dd, 1 H, $^3J_{3\text{-H, }4\text{-H}}$ = 14.9 Hz and $^3J_{3\text{-H, }2\text{-H}}$ = 10.8 Hz, 3-H),

6.45-6.52 (m, 2 H, 1/4-H), 6.85 - 6.93 (m, 2 H, 2/6-H), 7.45 (d, 2H, $^{3}J_{14\text{-H, }15\text{-H and }18\text{-H, }17\text{-H}}$ = 8.4 Hz, 14/18-H), 7.78 (d, $^{3}J_{15\text{-H, }14\text{-H and }17\text{-H, }18\text{-H}}$ = 8.3 Hz, 2H, 15/17-H).

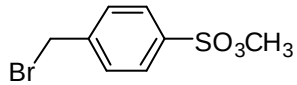
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 159.32 (s, C-8), 143.07 (s, C-13), 138.22 (s, C-16), 136.89 (d, C-1), 134.76 (d, C-6), 133.25 (d, C-2), 131.76 (d, C-5), 131.18 (d, C-3), 129.31 (d, C-4), 127.83 (d, C-14/18), 126.69 (d, C-15/17), 123.91 (d, C-7), 44.65 (q, S-CH_3), 39.10, 38.03 (s, C-9/11), 33.82, 31.74 (q, C-10/12).

IR (KBr): $\tilde{n}$ = 3002 cm^{-1} (m), 2960 (m), 2925 (m), 2909 (m), 1578 (m), 1320 (m), 1307 (O=S=O, s), 1146 (O=S=O, vs), 1123 (m), 1119 (m), 1112 (m), 1104 (m), 1091 (m), 1033 (m), 1029 (m), 1023 (m), 1017 (m), 1015 (m), 994 (m), 770 (m).

MS (70 eV): *m/z* (%) = 373 [M^++1] (17), 372 [M^+] (25), 332 (15), 315 [M^+- $C(CH_3)_3$] (100), 288 (20), 273 (10), 221 (10), 183 (20), 221 (9), 183 (20), 165 (9), 130 (13), 116 (26), 57 [$C(CH_3)_3$] (58).

UV ($CHCl_3$): λ_{max} (lg ε) = 268 nm (3.93), 334 (4.30), 344 (4.40), 366 (4.51), 378 (4.48).

4.3.48: 4-Bromomethyl-benzenesulfonic acid methyl ester (195)

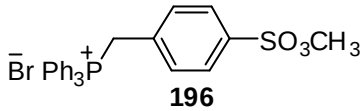


195

A stirred mixture of 2.00 g (10 mmol) of *p*-toluenesulfonic acid methylester **193**, 1.91 g (10 mmol) of NBS and a catalytic amount of AIBN in CCl_4 (40 mL) was refluxed for 5 h. After the reaction mixture reached to room temp. it was left stirring overnight. The mixture was filtered and the solvent of the mother liquor was evaporated in a rotary evaporator. The ^{1}H NMR spectrum of the crude mixture showed the presence of starting material **193** and the desired product **195** in 1:1 ratio. The starting material was removed from the product by kugelrohr distillation at 100 °C/0.03 mbar. The remaining compound in the distillation flask was the desired **195**. It was obtained in 49% yield (1.30 g, 4.9 mmol) as a grey solid.

The spectral data of compound **195** agree with the data given in ref.[72]

4.3.49: *p*-Bromobenzylsulfonicacid methylester (196)



196

A stirred mixture of 0.600 g (2.26 mmol) of **195** and 0.593 g (2.26 mmol) of triphenylphosphine in acetone (10 mL) was refluxed for 3 h. The clear light yellow solution turned turbid after starting the reflux, then formed a beige coloured precipitate. After the reaction had reached room temp. the precipate was filtered through a Büchner funnel and washed several times with acetone. **196** was dried at high vacuum: 0.647 g (54%, 1.22 mmol), white solid.

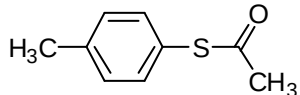
Compound **196** is completely insoluble in acetone, $CHCl_3$, Et_2O, CH_2Cl_2, CH_3CN, EtOAc, THF, H_2O, and its NMR and UV measurements could not be undertaken.

M.p. > 220 °C.

IR (KBr): $\tilde{n}$ = 3060 cm^{-1} (w), 2931 (w), 2891 (w), 1636 (w), 1588 (w), 1437 (s), 1227 (vs), 1194 (vs), 1183 (vs), 1121 (vs), 1113 (vs), 1036 (s), 1013 (vs), 748 (m), 691 (vs), 564 (m), 508 (m), 502 (m).

MS (70 eV): *m*/*z* (%) = 385 [Ph_3PCH_2PhS] (>1), 353 [Ph_3PCH_2Ph] (1), 294 (11), 293 [$PhPCH_2PhSO_3CH_3$] (11), 277 [Ph_3PCH_3] (100), 262 [PPh_3] (60), 199 (26), 183 [PCH_2PhSO_2] (68), 152 [$PhSO_2CH_3$] (21), 108 (26), 91 [$PhCH_2$] (4), 77 [C_6H_5] (4), 65 (3), 51 (4).

4.3.50: Thioacetic acid S-*p*-tolyl ester (199)



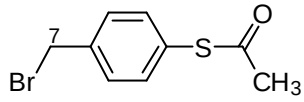
199

A mixture of 15 g (120 mmol) of *p*-thiocresol and 9.4 g (120 mmol) of acetylchloride in anhydrous benzene (250 mL) was stirred at 80 °C for 3 h under N_2. After the reaction had

reached room temp. again the solvent was evaporated and the product **199** was obtained in 77% yield (15.40 g, 92 mmol) as a colourless liquid. The compound was pure enough to be used for further reactions.

The spectral data of **199** are in accordance with the data given in ref.[73]

4.3.51: Thioacetic acid S-(4-bromomethyl-phenyl) ester (201)



201

A stirred suspension of 5 g (30mmol) of **199** and 5.16 g (18 mmol) of 3,3-dimethyl-*N*,*N*´-dibromo-hydantoin (**200**) in CCl_4 (60 mL) was irradiated with a 300 W sun lamp for 3 h under N_2. After about 15 min of irradiation all **200** had dissolved and the yellow colour of the suspension turned to dark red. After the reaction mixture cooled to room temp. the solvent was evaporated and the product was purified by column chromatography using CH_2Cl_2/pentane = 20:1 (v/v) as the eluent. The reaction yielded a mixture of two compounds: the desired compound **201** and the disulfide **202**. According to ^{1}H NMR analysis **201** was formed in 10% yield (0.743 g, 3 mmol) and the disulfide formed in 40% yield (3.28 g, 12 mmol). The compounds could not be separated from each other by chromatography completely. Both of them have the same R_F values (0.56 in CH_2Cl_2/pentane = 20:1). Different other solvent mixtures were also ineffective to separate the compounds. The mixture was hence directly used for further reaction.
The NMR data for **201** given below is from the NMR spectra of the mixture. The spectral data of **202** are known in the literature.[85]

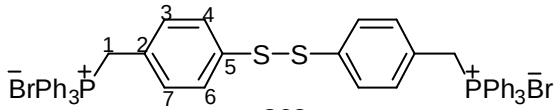
^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.31 (s, 3 H, CH_3), 4.44 (s, 2 H, 7-H), 7.29 - 7-31 (d, 2 H, ^3J = 8.3 Hz, Ar), 7.44-7.46 (d, 2 H, ^3J = 8.3 Hz, Ar).
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 137.81 (s), 137. 67 (s), 136. 56 (s), 129.74 (d), 127.67 (d), 32.86 (t, C-7), 21.03 (q).

IR (KBr): $\tilde{n}$ [cm^{-1}] = 3092 (w), 3070 (w), 3048 (w), 3020 (w), 2919 (w), 1594 (w), 1489 (vs), 1365 (m), 1225 (m), 1163 (m), 1077 (m), 1015 (m), 804 (vs).

MS (GC/MS): *m/z* (%) = 246 [M^+] (40), 213 , 198, 183, 182, 167 [M^+-Br], 154, 123 [M^+-Br-$HCOCH_3$] (100), 108, 97, 91, 89, 79, 77 [C_6H_5], 65, 51, 45.

UV (CH_3CN): λ_{max} (lg ε) = 204 nm (4.39), 244 (4.12), 256 (3.99), 260 (3.93), 278 (3.73), 300 (3.35), 322 (3.04).

4.3.52: 4-[(4-triphenylphosphoniummethyl)phenyldisulfanyl]benzyl triphenylphosphonium dibromide (203)



203

A stirred mixture of 0.743 g (3.02 mmol) of **202** and 0.792 g (3.02 mmol) of triphenylphosphine in acetone (10 mL) was refluxed for 3.5 h under N_2. With the inset of reflux formation of a white solid was observed. The reaction mixture was filtered and the white solid was washed several times, first with ether, then with acetone and finally dried under high vacuum: 0.817 g (70%, 1.06 mmol), a white solid.

M.p. 207-210 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.43 (d, 4 H, ^3J = 14.5 Hz, 1-H), 7.07 - 7.16 (m, 8 H, 3/4/6/7-H), 7.58 - 7.79 (m, 30 H).

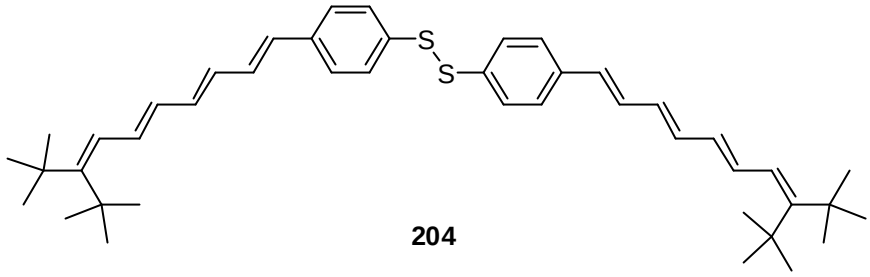
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 136.92 (s), 136.88 (s), 135.16 (d), 135.13 (d), 134.92 (d), 134.37 (d), 134.27 (d), 133.20 (d), 133.15 (d), 130.25 (d), 130.13 (d), 130.02 (d), 128.64 (s), 127.34 (d), 127.30 (d), 126.51 (s), 126.42 (s), 117.88 (s), 117.03 (s), 30.88 (t).

IR (KBr): $\tilde{n}$ = 3074 cm^{-1} (w), 3052 (w), 3006 (w), 2988 (w), 2852 (w), 1707 (w), 1623 (w), 1587 (w), 1489 (m), 1437 (vs), 1112 (vs), 744 (m), 723 (s), 690 (s), 536 (s), 502 (s).

MS (FAB positive): *m/z* (%) = 849 [M^+-Br] (40), 783 (17), 767 [M^+-2Br] (100), 691 (30), 626 (10), 549 (70), 507 (50), 384 [M^+-2Br-PPh_3] (80), 352 (17), 319 (17), 279 (40), 262 [PPh_3] (100), 183 (70), 154 (60), 136 (56), 123 (40), 91 (50), 81 (50), 77 [C_6H_6] (60), 69 (80), 55 (100), 41 (100).

UV ($CHCl_3$): λ_{max} (lg ε) = 196 nm (5.27), 226 (4.81), 232 (4.71), 270 (4.26), 278 (4.15 Although all the spectroscopic data are consistent with the proposed structure, elemental analysis of this substance did not yield satisfactory elemental composition.

4.3.53: 6-*tert*-butyl-7,7-dimethyl[4-[4-(6-*tert*-butyl-7,7-dimethylocta-1,3,5-trienyl)pheyldisulfanyl]phenyl]octa-1,3,5-triene (204)



204

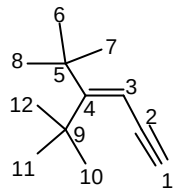
To a stirred suspension of 0.222 g (1.01 mmol) of **47b** and 0.500 g (1.01 mmol) of **203** in anhydrous THF (20 mL) was added 0.110 g (0.98 mmol) of *t*-BuOK under N_2. The yellow colour of the reaction turned immediately to very dark red. Controlling the reaction by TLC showed the disappereance of the starting material. The reaction was complete in less then 5 min. The reaction mixture was first hydrolyzed, then acidified (pH 5) with 1N HCl solution. The phases were separated and the aqueous phase was extracted several times with ether. The combined organic phases were dried with $MgSO_4$ and the solvent was evaporated. The remaining residue was purified by flash chromatography on silica gel using CH_2Cl_2/pentane = 3:20 (v/v) under N_2. An orange coloured solid, possibly the disulfide **204,** was obtained. Initial ^{1}H NMR and ^{13}C NMR measurements showed the presence of a mixture of isomers. The compound was highly unstable and in few h its orange colour changed to dark red and it became insoluble in the common organic solvents.

R_F (CH_2Cl_2/pentane = 3:20): 0.67.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.16 (s), 1.31 (s), 5.91 - 6.33 (m), 6.57 - 6.62 (m), 6.95 - 7.31 (m), 7.42 - 7.44 (d, ^3J = 8.1 Hz).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 183.15 (s), 162.88 (s), 141.22 (d), 137.3 (s), 136.97 (d), 130.95 (d), 129.78 (d), 129.73 (d), 129.44 (d), 129.29 (d), 128.48 (d), 127.92 (d), 123.81 (d), 123.67 (d), 39.10 (s), 38.15 (s), 33.88 (q) , 31.67 (q).

4.3.54: 4-*tert*-Butyl-5,5-dimethyl-hex-3-en-1-yne (207)



207

To a stirred suspension of 9.73 g (22.32 mmol) of bromomethyltriphenylphosphonium bromide **205** in anhydrous THF (80 mL) at −78 °C was added 2.5 g (22.32 mmol) *t*-BuOK under N_2, and the mixture was stirred for 30 min. With the ylid formation the colour changed from white to bright yellow. 3.00 g (17.85 mmol) of **114** in anhydrous THF (115 mL) was added dropwise at the same temperature and the mixture was left to warm up to room temp. Then 2.5 g (22.32 mmol) *t*-BuOK was added and the mixture was refluxed for 1.5 h. Another 1.25 g (11.16 mmol) *t*-BuOK was added and refluxing was continued for an additional 1.5 h. The reaction mixture was stirred overnight at room temp, quenched with water, and the phases were separated. The aqueous phase was extracted several times with diethylether, the combined organic phases were dried with anhydrous $MgSO_4$, and the sovent was removed in a rotary evaporator. The residue was purified by column chromatography on silica gel using hexane as the eluent. The acetylene **207** was obtained as a colourless highly volatile oil in 85% yield (2.49 g, 15 mmol).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.66 (d, 1 H, $J_{3\text{-H, }1\text{-H}}$ = 2.8 Hz, 3-H); 3.38 (d, 1 H, $J_{1\text{-H, }3\text{-H}}$ = 2.8 Hz, 1-H); 1.51 and 1.47 (s, 18 H, *t*-Bu).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 171.40 (s, C-4); 103. 37 (d, C-3); 85.87 (s, C-2), 84.34 (d, C-1), 39.50 and 38.85 (s, C-5/9), 32.29, 31.56 (q, *t*-Bu).

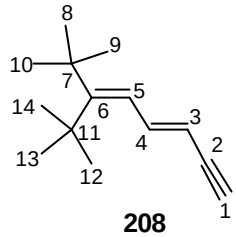
IR (Film): $\tilde{n}$ = 3314 cm^{-1} (m), 2958 (s), 2090 (C≡C, w), 1729 (w), 1485 (C=C, w), 1366 (m), 1237 (m), 1219 (m), 1196 (m), 835 (w).

MS (GC/MS): *m/z* (%) =164 [M^+], 149, 135, 121, 107 [M^+- $C(CH_3)_3$], 99, 91, 79, 65, 57 [$C(CH_3)_3$].

UV (CH_3CN): λ_{max} (lg ε) = 234 nm (4.02), 260 (3.36).

Although all the spectroscopic data are consistent with the proposed structure elemental analysis of this substance did not yield satisfactory elemental composition.

4.3.55: 6-*tert*-Butyl-7,7-dimethyl-octa-3,5-dien-1-yne (208)



208

To a stirred suspension of 4.51 g (10.00 mmol) bromomethyl-triphenyl-phosphonium bromide **205** in anhydrous THF (25 mL) at −78 °C was added 1.16 g (10.00 mmol) of *t*-BuOK under N_2, and the mixture was stirred for 30 min. With the ylid formation the colour changed from white to bright yellow. 1.00 g (5.18 mmol) of **47a** in anhydrous THF (10 mL) was added dropwise at the same temperature and the mixture was left to warm up to room temp. Then 1.74 g (10.00 mmol) *t*-BuOK was added and the mixture was first refluxed for 3h followed by overnight stirring at room temp. The reaction was quenched by addition of water, and the phases were separated. The aqueous phase was extracted several times with diethylether, the combined organic phases were dried with anhydrous $MgSO_4$, and the sovent was removed in a rotary evaporator. The residue was purified by column chromatography on silica gel using hexane as the eluent. The acetylene **208** was obtained as a colourless oil in 85% yield (0.836 g, 4.40 mmol).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.36, 1.22 (s, 18 H, *t*-Bu), 3.03 (d, 1 H, $J_{1\text{-H, }3\text{-H}}$ = 1.9 Hz, 1-H), 5.41 (dd, 1 H, $J_{3\text{H-4H}}$ = 15.2 Hz, $J_{3\text{-H, }1\text{-H}}$ = 2.0 Hz, 3-H), 6.02 (d, 1 H, $J_{1\text{H-3H}}$ = 11.6 Hz, 5-H), 7.33 (dd, 1 H, $J_{4\text{-H, }3\text{-H}}$ = 15.2 Hz., $J_{4\text{-H, }5\text{-H}}$ = 11.6 Hz, 4-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 142.81 (d, C-4); 122.78 (d, C-5); 108.55 (d, C-3); 84.00 (s, C-2); 78.97 (d, C-1); 39.09, 38.06 (s, C-7/14); 33.91, 31.59 (q, C-9/ 14).

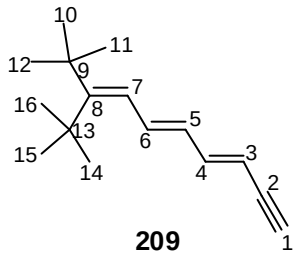
IR (Film): $\tilde{n}$ = 2929 cm^{-1} (s), 2039 (C≡C, w), 1637 (C=C, m), 1380 (m), 1254 (m), 1201 (m), 1172 (m).

MS (GC/MS): *m*/*z* (%) = 190 [M^+] (13), 133 [M^+-$C(CH_3)_3$] (66), 119 (57), 105 (57), 91 (68), 84 (10), 77 (16), 69 (13), 57 [$C(CH_3)_3$] (100).

UV (CH_3CN): λ_{max} (lg ε) = 222 nm (3.70), 276 (4.30), 286 (4.24)[sh], 288 (4.23), 304 (3.54).

Although all the spectroscopic data are consistent with the proposed structure, elemental analysis of this substance did not yield satisfactory elemental composition.

4.3.56: 8-*tert*-Butyl-9,9-dimethyl-deca-3,5,7-trien-1-yne (209)



209

To a stirred suspension of 3.76 g (8.63 mmol) of bromomethyl-triphenyl-phosphonium bromide **205** in anhydrous THF (22 mL) at −78 °C was added 0.960 g (8.60 mmol) of *t*-BuOK under N_2 and the mixture was stirred for 30 min. With the ylid formation the colour changed from white to bright yellow. 1.00 g (4.54 mmol) of **47b** in anhydrous THF (10 mL) was added dropwise at the same temperature and the mixture was left to warm up to room temp. Then 1.45 g (12.90 mmol) of *t*-BuOK was added and the mixture was first refluxed for 3h followed by overnight stirring at room temp. The reaction was quenched by addition of water, and the phases were separated. The aqueous phase was extracted several times with diethylether, the combined organic phases were dried with anhydrous $MgSO_4$, and the sovent was removed in a rotary evaporator. The residue was purified by column chromatography on silica gel using hexane as the eluent. The acetylene **209** was obtained as a colourless oil in 80% yield (0.790 g, 3.63 mmol).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 6.86 (dd, 1 H, $J_{4\text{-H, }3\text{-H}}$ = 14.4 Hz, $J_{6\text{-H, }7\text{-H}}$ = 11.7 Hz, 6-H), 6.70 (dd, 1 H, $J_{4\text{-H, }3\text{-H}}$ = 15.5 Hz, $J_{4\text{-H, }5\text{-H}}$ = 11.1 Hz, 4-H), 6.04 (dd, 1,H, $J_{5\text{-H, }6\text{-H}}$ = 14.4 Hz, $J_{5\text{-H, }4\text{-H}}$ = 11.1 Hz, 5-H), 5.97 (d, 1 H, $J_{7\text{-H, }6\text{-H}}$ = 11.7 Hz, 7-H), 5.46 (dd, 1 H, $J_{3\text{-H, }4\text{-H}}$ = 15.5 Hz, $J_{3\text{-H, }1\text{-H}}$ = 2.4 Hz, 3-H), 2.98 (d, 1 H, $J_{1\text{-H, }3\text{-H}}$ = 2.4 Hz, 1-H), 1.29 and 1.15 (s, 18H, *t*-Bu).

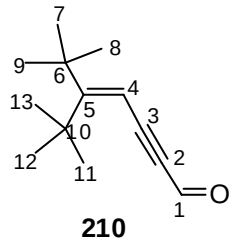
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 160.55 (s, C-8); 144.38 (d, C-6); 135.75 (d, C-4); 130.84 (d, C-7); 123.74 (d, C-5); 108.71 (d, C-3); 83.86 (s, C-2); 80.01 (d, C-1); 39.43 and 38.34 (s, C-9/13); 34.10 and 32.01 (q, C-10/16).

IR (Film): $\tilde{n}$ = 3312 cm^{-1} (m), 2957 (s), 2094 (C≡C, w), 1598 (C=C, m), 1484 (m), 1459 (m), 1366 (m), 1217 (m), 988 (s).

UV (CH_3CN): λ_{max} (lg ε) = 242 nm (3.62), 288 (4.30), 310 (4.60), 322 (4.58), 350 (3.97), 364 (2.91).

During spectrometric analysis the compound polymerized.

4.3.57: 5-*tert*-Butyl-6,6-dimethyl-hept-4-en-2-ynal (210)



210

n-BuLi (6.10 mL, 1.6 M solution in hexane) was slowly added to a stirred solution of 1.0 g (6.1 mmol) of **207** in anhydrous diethylether (40 mL) at −78 °C. The colourless solution turned red. The mixture was left to warm up to room temp. slowly, then cooled back to −78 °C, and DMF (0.79 mL, 1 mmol) was added. After letting the reaction mixture warm to room temp. again, stirring was continued overnight. The reaction mixture was quenched by addition of water and the layers were separated. The aqueous phase was extracted several times with diethylether, the combined organic layers were dried with anhydrous $MgSO_4$ and the solvent was removed in a rotary evaporator. The remaining

residue was purified by column chromatography on silica gel using ethyl acetate/hexane = 1:10 (v/v) as the eluent. Aldehyde **210** was obtained as a red oil in 85 % yield (1.00 g, 5.185 mmol). Besides, 10% (0.159 g, 0.61 mmol) of 2-(1-*tert*-Butyl-2,2-dimethyl-propylidne)-non-5-en-3-ynal (**211**) was obtained as a side product.

In an other experiment 0.47 g (3.66 mmol) of freshly prepared EtMgBr in THF (3 mL) was added slowly to a cooled solution (- 40 °C) of 0.5 g (3.05 mmol) of **207** in THF (5 mL) under N_2. First white, then gray suspension formation was observed. Reaction was left to warm to room temp. and stirred for an additional 1 h, then cooled to – 30 °C and 0.267 g (3.66 mmol) of DMF in THF (2 mL) was added. Stirring was continued overnight at room temp. The reaction mixture was quenched by addition of water and the layers were separated. The aqueous phase was extracted several times with diethylether, the combined organic layers were dried with anhydrous $MgSO_4$ and the solvent was removed. After chromatographic purification (see above) **210** was obtained in 85 % yield (0.497 g, 2.5 mmol).

5-*tert*-Butyl-6,6-dimethyl-hept-4-en-2-ynal (210)

R_F (EtOAc/hexane = 1:10): 0.76.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.47, 1.24 (s, 18 H, *t*-Bu), 5.80 (d, 1 H, $J_{4\text{-H, }1\text{-H}}$ = 1.0 Hz, 4-H), 9.36 (d, 1 H, $J_{1\text{-H, }4\text{-H}}$ = 1.2 Hz, 1-H)

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 179.79 (s, C-5), 176.87 (d, C-1), 101.65 (d, C-4), 97.06, 96.01 (s, C-2/3), 40.02, 39.46 (s, C-6/10), 32.35, 31.02 (q, C-7/13).

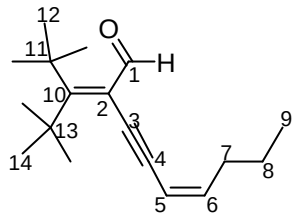
IR (Film): $\tilde{n}$ = 2960 cm^{-1} (m), 2164 (C≡C, s), 1660 (C=O, s), 1569 (C=C, w), 1485 (w), 1367 (w), 1152 (m).

MS (70 eV): *m/z* (%) = 192 [M^+] (2), 136 (34), 121 (13), 105 (11), 92 (28), 91 (32), 84 (28), 79 (11), 77 (15), 69 (17), 65 (10), 57 [$C(CH_3)_3$] (100).

UV (CH_3CN): λ_{max} (lg ε) = 198 nm (3.83), 216 (3.86), 292 (4.01), 328 (3.27), 334 (3.11), 344 (2.93), 356 (2.73).

Although all the spectroscopic data are consistent with the proposed structure elemental analysis of this substance did not yield satisfactory elemental composition. The intensity of the molecular ion peak was too small to carry out a HRMS measurement.

2-(1-*tert*-Butyl-2,2-dimethyl-propylidne)-non-5-en-3-ynal (211)



211

R_F (EtOAc/hexane = 1:10): 0.66.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.85 (t, 5 H, 8/9-H), 1.18, 1.41 (s, 18 H, 12/14-H), 2.35 (m, 2 H, 7-H), 5.82 (d, 1 H, $^3J_{5\text{-H, }6\text{-H}}$ = 3.0 Hz, 5-H), 6.45 (d, 1 H, $^3J_{6\text{-H, }5\text{-H}}$ = 3.0 Hz, 6-H), 9.4 (s, 1 H, 1-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 193.96 (d, C-1), 173.07 (s, C-10), 150.53 (s, C-2), 130.32 (d, C-6), 103. 74 (d, C-5), 39.58, 38.90 (s, C-11/13), 32.16, 31.16 (q, C-12/14), 28.22 (t, C-7), 21.93 (t, C-8), 13.96 (q, C-9).

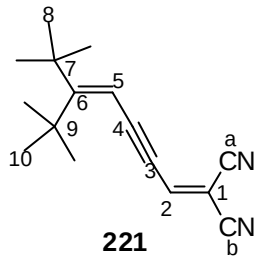
IR (Film): $\tilde{n}$ = 2960 cm^{-1} (vs), 2931 (s), 2873 (s), 2167 (C≡C, s), 1683 (C=O, vs), 1665 (s), 1604 (w), 1561 (w), 1485 (w), 1392 (m), 1366 (s), 1187 (m).

MS (70 eV): *m*/*z* (%) = 260 (30) [M^+], 203 (94) [M^+- $C(CH_3)_3$], 189 (26), 175 (25), 161 (62), 147 (46), 133 (48), 131 (37), 119 (90), 117 (14), 105 (26), 91 (34), 84 (9), 77 (18), 69 (14), 57 (100) [$C(CH_3)_3$], 55 (20).

HRMS $C_{18}H_{28}O$ (260.41) Calc. 260.2140

Found 260.2133 ± 2ppm

4.3.58: 2-(5-*tert*-Butyl-6,6-dimethyl-hept-4-en-2-ynylidne)-malononitrile (221):



221

A mixture of 0.1 g (0.52 mmol) **210**, 0.034 g (0.52 mmol) malononitrile and a catalytic amount of 0.001 g (0.11 mmol) *b*-alanine in 95% EtOH was stirred for 30 min at room temp. The mixture was diluted with water and extracted several times with diethylether. The combined organic phases were dried with $MgSO_4$ and the solvent was removed in vacuo. The remaining residue was purified by column chromatography on silica gel using diethylether/pentane = 1:2 (v/v) as the eluent. Compound **221** was obtained as a greenish yellow oil in 100 % yield (0.124 g, 5.20 mmol).

R_F (Et_2O:pentane = 1/2): 0.64.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.48, 1.26 (s, 18 H, 8/10-H), 5.97 (d, 1 H, $J_{5\text{-H, }2\text{-H}}$ = 3.3 Hz, 5-H), 7.11 (d, 1 H, $J_{2\text{-H, }5\text{-H}}$ = 3.3 Hz, 2-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 182.01 (s, C-6), 141.70 (d, C-2), 116.35, 112.83, 111.73 (s, C-1/a/b), 102.78 (d, C-5), 93.34, 91.46 (s, C-3/4), 40.38, 39.86 (s, C-7/9), 32.55, 30.97 (q, 8/10).

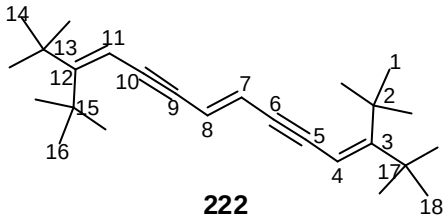
IR (Film): $\tilde{n}$ = 2962 cm^{-1} (m), 2233 (C≡N, w), 2158 (C≡C, s), 1537 (C=C, s), 1485 (w), 1367 (w), 1198 (w), 992 (w), 674 (w).

MS (70 eV): *m/z* (%) = 240 [M^+] (4), 184 (40), 169 (18), 157 (7), 140 (8), 128 (7), 115 (6), 84 (27), 69 (12), 57 [$C(CH_3)_3$] (100).

UV (CH_3CN): λ_{max} (lg ε) = 218 nm (3.92), 306 (3.93), 322 (4.01), 362 (4.28), 418 (2.81).

Elemental analysis $C_{16}H_{20}N_2$ (240.4) Calc. C 79.96% H 8.39% N 11.66%
Found C 79.82% H 8.37% N 11.09%

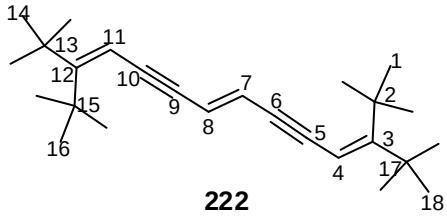
4.3.59: all-*trans*-3,12-Di-*tert*-butyl-2,2,13,13-tetramethyl-tetradeca-3,7,11-triene-5,9-diyne (222)



222

To anhydrous THF (5 mL) cooled to 0 °C, first 0.218 g (1.146 mmol) of $TiCl_4$ was added under nitrogen, followed by 0.155 g (2.375 mmol) of Zn powder and finally 0.076 g (0.958 mmol) of pyridine. The dark gray mixture was stirred for 30 min, then 0.200 g (1.04 mmol) of **210** in THF (5 mL) was added dropwise. Cooling was removed immediately and the reaction was refluxed for 15 min. The mixture was quenched by addition of 1N aqueous HCl which dissolved the black precipitate completely. After extraction with ether the organic phase was neutralized with saturated $NaHCO_3$ solution, the layers were separated, and the organic layer was dried with $MgSO_4$. The solvent was removed in a rotary evaporator and the residue was purified by column chromatography on silica gel with hexane: 0.153 g (0.436 mmol, 42%) of **222**. Besides, a 1:1 ratio of (7*Z*)-3,12-di-*tert*-butyl-2,2,13,13-tetramethyl-tetradeca-3,7,11-triene-5,9-diyne (**223)** and 3-(2-*tert*-butyl-3,3-dimethyl-but-1-enyl)-2-(4-*tert*-butyl-5,5-dimethyl-hex-3-en-1-ynyl)furan (**224)** were formed as side products.

all-*trans*-3,12-Di-*tert*-butyl-2,2,13,13-tetramethyl-tetradeca-3,7,11-triene-5,9-diyne (222)



222

R_F (hexane): 0.74.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.21, 1.44 (s, 36 H, 1/14/16/18-H), 5.76 (s, 2 H, 4/11-H), 6.09 (s, 2 H, 7/8-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.35 (s, C-3/15), 119.68 (d, C-7/8), 103.87 (d, C-4/11), 96.50 (s, C-6/9), 95.12 (s, C-5/10), 39.34, 38.73 (s, C-2/13/15/17), 32.13, 31.32 (q, C-1/14/16/18).

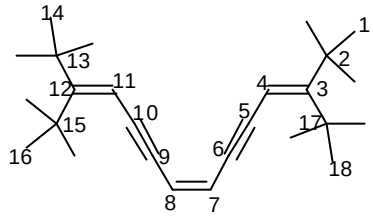
IR (KBr): $\tilde{n}$ = 2956 cm^{-1} (vs), 2186 (C≡C, m), 1484 (m), 1467 (m), 1397 (m), 1365 (m), 1236 (m), 1197 (m), 1179 (m), 928 (m).

UV ($CHCl_3$): λ_{max} (lg ε) = 318 nm (4.42, sh), 332 (4.50), 334 (4.49), 352 (4.36, sh).

MS (70 eV): *m/z* (%) = 352 [M^+] (65), 295 [M^+-$C(CH_3)_3$] (63), 209 (11), 193 (16), 181 (14), 169 (26), 165 (12), 145 (20), 143 (9), 129 (11), 119 (21), 105 (13), 91 (12), 57 [$C(CH_3)_3$] (100).

HRMS $C_{26}H_{40}$ (352.60) Calc. 352.3130
Found 352.3120 ±2 ppm

(7*Z*)-3,12-di-*tert*-butyl-2,2,13,13-tetramethyl-tetradeca-3,7,11-triene-5,9-diyne (223)



223

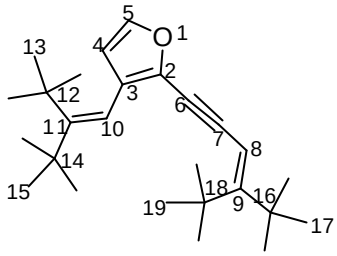
R_F (hexane): 0.64

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.15, 1.41 (s, 36 H, 1/14/16/18-H), 5.74 (s, 2 H, 4/11-H), 5.84 (d, 2 H, ^3J = 1 Hz, 7/8-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 169.9 (s, C-3/12), 118 (d, C-7/8), 104.35 (d, C-4/11), 97.25 (s, C-6/9), 95.82 (s, C-5/10), 39.34, 38.69 (s, C-2/13/15/17), 32.15, 31.33 (q, C-1/14/16/18).

MS (GC/MS): *m/z* (%) = 352 [M^+] (10), 295 [M^+-$C(CH_3)_3$] (20), 281, 265, 239, 223, 211, 193, 181, 169 (20), 156, 145 (10), 133, 119 (20), 105 (10), 91, 79, 69, 57 [$C(CH_3)_3$] (100).

3-(2-*tert*-butyl-3,3-dimethyl-but-1-enyl)-2-(4-*tert*-butyl-5,5-dimethyl-hex-3-en-1-ynyl)furan (224)



224

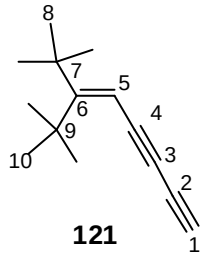
R_F (hexane): 0.64.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.15, 1.18, 1.20, 1.41 (s, 36 H, 13/15/17/19-H), 5.79 (s, 1 H, 8-H), 6.17 (s, 1 H, 10-H), 6.25 (d, 1 H, $^3J_{4\text{-H},\,5\text{-H}}$ = 1.9 Hz, 4-H), 7.21 (s, 1 H, $^3J_{5\text{-H},\,4\text{-H}}$ = 1.9 Hz, 5-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 169.1 (s, C-9), 159.9 (s, C-11), 142 (d, C-5), 129 (s, C-2/3), 114.89 (d, C-10), 114.1 (d, C-4), 103.44 (d, C-8), 96.64 (s, C-7), 87.77 (s, C-6), 39.51, 39.34, 39.28, 38.74 (s, C-12/14/16/18), 32.32, 32.34, 33.48 (q, C-13/15/17/19).

MS (GC/MS): *m/z* (%) = 368 [M^+], 312, 297, 281, 269, 255, 241, 227, 199 (10), 185 (40), 171, 151, 133, 119, 109 (10), 95 (30), 83, 69, 57 [$C(CH_3)_3$] (100).

4.3.60: 6-*tert*-Butyl-7,7-dimethyl-oct-5-ene-1,3-diyne (121)



121

To a suspension of 1.00 g (2.27 mmol) of bromomethyl-triphenylphosphonium bromide **215** in THF (8 mL) cooled to –78 °C, 0.255 g (2.27 mmol) of *t*-BuOK was added under N_2 and the mixture was stirred for 30 min, 0.350 g (1.82 mmol) of the aldehyde **210** in THF (12 mL) was added dropwise and the mixture was left to reach room temp. Then 0.255 g (2.27 mmol) of *t*-BuOK was added and the mixture was refluxed for 3 h. Stirring was continued overnight at room temp. The reaction mixture was hydrolyzed with 20 mL

of water and the phases were separated. The aqueous phase was extracted several times with diethylether. The combined organic phases were dried with $MgSO_4$, and the sovent was removed in a rotary evaporator. The remaining residue was purified by column chromatography on silica gel with pentane. After purification 0.184 g (0.98 mmol, 54%) of **121** was obtained. The compound was observed to be highly unstable and polymerized to some extent during purification already, making it impossible to determine its elemental composition.

R_F (pentane): 0.66.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.45 and 1.20 (s, 18 H, 8/10-H), 2.58 (d, 1 H, $J_{1\text{-H, }5\text{-H}}$ = 1.2 Hz, 1-H), 5.65 (d, 1 H, $J_{5\text{-H, }1\text{-H}}$ = 1.0 Hz, 5-H).

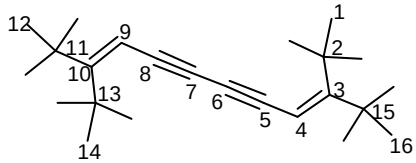
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 175.83 (s, C-6), 102.16 (d, C-5), 81.36 (s, C-4), 75.25, 72.63 (s, C-2/3/4), 68.67 (d, C-1), 39.49, 39.07 (s, C-7/9); 32.27 and 31.14 (q, C-8/10).

IR (KBr): $\tilde{n}$ = 3312 cm^{-1} (m), 2959 (s), 2186 (C≡C, m), 1571 (C=C, w), 1484 (m), 1366 (m), 1233 (m), 1214 (m), 1195 (m), 665 (w).

MS (70 eV): *m*/*z* (%) = The compound ($C_{14}H_{20}$, M^+ = 188) gave the mass spectrum of the coupled product (see Exp. 4.3.64); 374 [2×M^+-2H] (24), 317 [2×M^+-$C(CH_3)_3$] (16), 245 (12), 229 (14), 215 (20), 191 (14), 177 (14), 157 (14), 141 (12), 119 (14), 109 (10), 91 (18), 83 (10), 57 [$C(CH_3)_3$] (100).

UV ($CHCl_3$): λ_{max} (lg ε) = 214 nm (4.16), 220 (4.19), 250 (3.79), 260 (3.91), 274 (4.02), 290 (4.00), 308 (3.69), 328 (3.52), 348 (3.31), 364 (3.14), 378 (3.08), 412 (2.81).

4.3.61: 3,10-Di-*tert*-butyl-2,2,11,11-tetramethyl-dodeca-3,9-diene-5,7-diyne (227)



227

Oxygen gas was bubbled for 2 h through a stirred suspension of 0.923 g (5.63 mmol) of **207** and 0.167 g (1.69 mmol) of Cu(I)Cl in 15 mL of pyridine. The pyridine was removed

in vacuo, the remaining precipitate was dissolved by the addition of aqueous NH_4Cl solution and extracted several times with diethyl ether. The combined organic phases were dried with $MgSO_4$ and the solvent was removed in a rotary evaporator. The crude mixture was first filtered through silica gel using hexane as the eluent, then purification was completed by sumblimation at 75 °C/ 4 mbar. The compound was obtained in 100% yield (0.915 g, 2.81 mmol) as a yellow solid.

R_F (hexane): 0.71

M.p. 105-106 °C

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.45 and 1.20 (s, 36 H, 1/12/14/16-H), 5.76 (s, 2 H, 4/9-H)

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 173.17 (s, C-3/13), 103.24 (d, C-4/9), 83.13 (s, C-6/7); 82,7 (s, C-5/8); 39.41 and 38.95 (s, C-2/11/13/15), 32.25, 31.25 (q, 1/12/14/16).

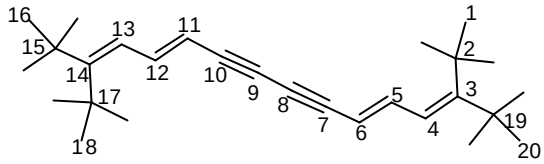
IR (KBr): $\tilde{n}$ = 2953 cm^{-1} (s), 2120 (C≡C, w), 1561 (C=C, w), 1482 (m), 1387 (m), 1362 (s), 1216 (s), 829 (m), 664 (m).

MS (70 eV): *m*/*z* (%) = 326 [M^+] (50), 270 (16), 269 [M^+-$C(CH_3)_3$] (68), 213 (19), 197 (24), 185 (27), 171 (17), 167 (12), 157 (18), 143 (35), 133 (11), 128 (19), 119 (50), 107 (19), 57 [$C(CH_3)_3$] (100).

UV ($CHCl_3$): λ_{max} (lg ε) = 194 nm (4.15), 202 (4.15), 208 (4.16), 216 (4.24), 238 (4.48), 246 (4.53), 252 (4.55), 264 (4.49), 276 (4.01), 294 (4.23), 312 (4.41), 332 (4.32).

Elemental analysis $C_{24}H_{38}$ (326.6) Calc. C 88.27% H 11.73%
Found C 88.19% H 11.70%

4.3.62: 3,14-Di-*tert*-butyl-2,2,15,15-tetramethyl-hexadeca-3,5,11,13-tetraene-7,9-diyne (228)



228

Oxygen gas was passed for 2 h through a stirred suspension of 0.200 g (1.05 mmol) of **208** and 0.031 g (0.315 mmol) of Cu(I)Cl in 15 mL of pyridine. The pyridine was removed in vacuo, the remaining precipitate was dissolved by the addition of aqueous NH_4Cl solution and extracted several times with diethyl ether. The combined organic phases were dried with $MgSO_4$ and the solvent was removed in a rotary evaporator. The crude mixture was first filtered through silica gel using hexane as the eluent, then purification was completed by sumblimation at 120 °C/ 4 mbar. The compound was obtained in 0.179 g (0.50 mmol, 95%) as a yellow solid.

R_F (hexane): 0.92.

M.p. 136 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.36, 1.22 (s, 36 H, 1/16/18/20-H), 5.53 (d, 2 H, $J_{6\text{-H, }5\text{-H and }11\text{-H, }12\text{-H}}$ = 14.9 Hz, 4/9-H), 6.06 (d, 2 H, $J_{4\text{-H, }5\text{-H and }13\text{-H, }12\text{-H}}$ = 11.8 Hz, 4/13-H), 7.39 (dd, 2 H, $J_{5\text{-H, }6\text{-H and }12\text{-H, }11\text{-H}}$ = 14.9 Hz, $J_{5\text{-H,}4\text{-H and }12\text{-H, }13\text{-H}}$ = 11.8 Hz, 5/12-H);

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 162.08 (s, C-3/14), 144.13 (d, C-5/12), 123.07 (d, C-4/13), 108.56 (d, C-6/11), 83.22 (s, C-8/9), 77.20 (s, C-7/10), 39.26, 38.26 (s, C-2/15/17/19), 33.98, 31.58 (q, C-1/16/18/20).

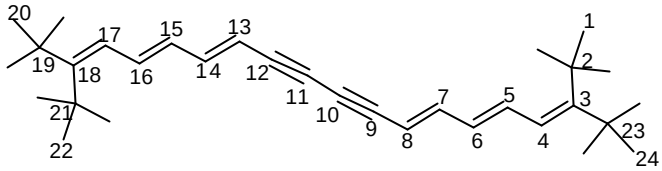
IR (KBr): $\tilde{n}$ = 3037 cm^{-1} (w), 2935 (s), 2135 (C≡C, w), 1605 (C=C, m), 1461 (m), 1378 (m), 1196 (s), 953 (s), 739 (m).

MS (70 eV): *m/z* (%) = 378 [M^+] (86), 321 [M^+-$C(CH_3)_3$] (6), 265 (10), 249 (17), 235 (14), 222 (13), 207 (15), 194 (16), 179 (10), 145 (16), 133 (11), 57 [$C(CH_3)_3$] (100).

UV ($CHCl_3$): λ_{max} (lg ε) = 218 nm (3,85), 222 (3.89), 248 (3.80), 262 (3.90), 276 (4.01), 292 (4.04), 314 (4.10), 328 (4.16), 336 (4.18), 358 (4.28), 384 (4.23).

Elemental Analysis $C_{28}H_{42}$ (378.7) Calc. C 88.82% H 11.18%
Found C 88.66% H 11.30%

4.3.63: 3,18-Di-*tert*-butyl-2,2,19,19-tetramethyl-icosa-3,5,7,13,15,17-hexaene-9,11-diyne (229)



229

Oxygen gas was passed for 2 h through a stirred suspension of 0.100 g (0.463 mmol) of **209** and 0.014 g (0.140 mmol) of Cu(I)Cl in 5 mL of pyridine. The pyridine was removed in vacuo, the remaining precipitate was dissolved by the addition of aqueous NH_4Cl solution and extracted several times with diethyl ether. The combined organic phases were dried with $MgSO_4$ and the solvent was removed in a rotary evaporator. The remaining residue was purified by column chromatography on silica gel using hexane as the eluent. The diacetylene **229** was obtained in 98 mg (0.23 mmol, 98%) as a yellow solid.

R_F (hexane): 0.46.

M.p. 148 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.29, 1.15 (s, 36 H, 1/20/22/24-H), 5.58 (d, 2 H, $J_{8\text{-H, 7-H and 13-H, 14-H}}$ = 15.1 Hz, 8/13-H), 5.98 (d, 2 H, $J_{4\text{-H, 5-H and 17-H, 16-H}}$ = 11.8 Hz, 4/17-H), 6.07 (dd, 2 H, $J_{6\text{-H, 5-H and 15-H, 16-H}}$ = 14.3 Hz, $J_{6\text{-H, 7-H and 15-H, 14-H}}$ = 11.3 Hz, 6/15-H), 6.74 (dd, 2 H, $J_{7\text{-H, 8-H and 14-H, 13-H}}$ = 15.4 Hz, $J_{7\text{-H, 6-H and 14-H, 15-H}}$ = 11.3 Hz, 7/14-H), 6.89 (dd, 2 H, $J_{5\text{-H, 6-H and 16-H, 15-H}}$ = 14.3 Hz, $J_{5\text{-H, 4-H and 16-H, 17-H}}$ = 11.8 Hz, 5/16-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 161.03 (s, C-3/18), 145.18 (d, C-5/16), 136.10 (d, C-7/14), 130.81 (d, C-6/15), 123.57 (d, C-4/17), 108.45 (d, C-8/13), 84.03 (s, C-10/11), 77.46 (s, C-9/12), 39.20, 38.13 (s, C-2/19/21/23), 33.87, 31.67 (q, C-1/20/22/24).

IR (KBr): $\tilde{n}$ = 3064 cm^{-1} (w), 2957 (s), 2115 (C≡C, w), 1586 (C=C, m), 1480 (w), 1367 (m), 1280 (w), 1216 (m), 986 (s).

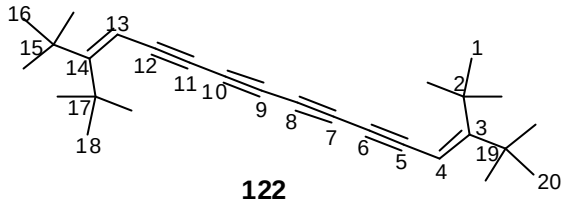
MS (70 eV): *m*/*z* (%) = 430 [M^+] (86), 317 (15), 301 (4), 289 (5), 274 (5), 261 (7), 246 (8), 232 (12), 219 (5), 205 (7), 171 (7), 117 (7), 61 (12), 57 [$C(CH_3)_3$] (100).

UV ($CHCl_3$): λ_{max} (lg ε) = 268 nm (4.22), 296 (4.30), 308 (4.37), 318 (4.45), 338 (4.52), 370 (4.78), 392 (4.82), 422 (4.76).

HRMS $C_{32}H_{46}$ (430.7) Calc. 430.3599

Found 430.3588 ± 2ppm

4.3.64: 3,14-Di-*tert*-butyl-2,2,15,15-tetramethyl-hexadeca-3,13-diene-5,7,9,11-tetrayne (122)



122

Oxygen gas was bubbled for 1 h through a stirred suspension of 40 mg (0.213 mmol) of **121** and 6 mg (0.069 mmol) of Cu(I)Cl in pyridine (5 mL). The pyridine was removed in vacuo and the remaining precipitate was dissolved by addition of aqueous NH_4Cl solution. The mixture was extracted several times with diethyl ether, the combined organic phases were dried with $MgSO_4$, and the solvent was removed in a rotary evaporator. After purification of the remaining residue by column chromatography on silica gel using hexane 26 mg (0.069 mmol, 65%) of **122** was obtained, yellow solid.

R_F (hexane): 0.46.

M.p. 124 °C

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.35, 1.20 (s, 36 H, 1/16/18/20-H), 5.64 (s, 2 H, 4/13-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ =178.34 (s, C-3/15), 101.99 (d, C-4/13), 82.29, 77.81, 69.10, 64.84 (s, C-5/6/7/8/9/10/11/12), 39.72, 39.43 (s, C-2/15/17/19), 32.40, 31.11 (q, C-1/16/18/20).

IR (KBr): $\tilde{n}$ = 2958 cm^{-1} (s), 2179 (C≡C, s), 1559 (C=C, m), 1483 (m), 1466 (m), 1391 (m), 1231 (m), 1195 (m), 1049 (m), 992 (m), 992 (m), 825 (m).

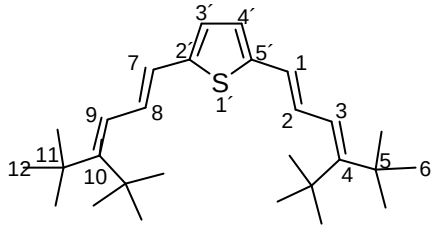
MS (70 eV): *m/z* (%) = 374 [M^+] (63), 317 [M^+-$C(CH_3)_3$] (51), 287 (6), 259 (7), 245 (26), 231 (32), 229 (27), 215 (38), 191 (24), 189 (15), 165 (12), 155 (10), 143 (9), 129 (13), 119 (12), 91 (8), 57 [$C(CH_3)_3$] (100).

UV ($CHCl_3$): λ_{max} (lg ε) = 208 nm (4.29), 216 (4.28), 236 (4.34), 246 (4.45), 254 (4.57), 262 (4.61),, 282 (4.76), 296 (4.93), 314 (4.83), 330 (4.19), 354 (4.23), 380 (4.28), 412 (4.07).

HRMS $C_{28}H_{38}$ (374.6) Calc. 374.2973

Found 374.2964 ± 2ppm

4.3.65: 2,5-Bis-(4-*tert*-butyl-5,5-dimethyl-hexa-1,3-dienyl)-thiophene (230)



230

A stirred mixture of 40 mg (0.105 mmol) of **228**, 56 mg (0.233 mmol) of $Na_2S{\cdot}9H_2O$ and 12 mg (0.211 mmol) of KOH in DMSO (25 mL) was heated to 55 °C. The progress of the reaction was monitored by TLC and after 10 min conversion of **228** to the product was complete. The DMSO was removed by vacuum distillation, the remaining residue was dissolved by addition of water and the mixture was extracted several times with diethyl ether. The combined organic phases were dried with $MgSO_4$ and the solvent was removed by rotary evaporatoion. After purification of the remaining residue by column chromatography on silica gel with ethyl acetate/hexane = 1:10 (v/v), the thiophene derivative **230** was obtained in 100% yield (43 mg, 0.105 mmol) as a yellow solid.

R_F (EtOAC/hexane = 1:10): 0.89.

M.p. 159 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.36, 1.17 (s, 36 H, 6/12/14/16-H), 6.03 (dd, 2 H, $^3J_{3\text{-H, 2-H and 9-H, 8-H}}$ = 11.4 Hz, 3/9-H), 6.38 (dd, 2 H, $^3J_{1\text{-H, 2-H and 7-H, 8-H}}$ = 14.9 Hz, 1/7-H), 6.69

(s, 2H, 3´/4´-H), 7.06 (dd, 2 H, $^3J_{2\text{-H, 1-H and 8-H, 7-H}}$ = 14.9 Hz, $^3J_{2\text{-H, 3-H and 8-H, 9-H}}$ = 11.4 Hz, 2/8-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 157.82 (s, C-4/10), 142.11 (s, C-2´/5´), 128.40 (d, C-2/8); 126.22 (d, C-3´/4´), 124.52 (d, C-1/7), 123.59 (d, C-3/9), 39.02, 38.00 (s, C-5/11/13/15), 33.99, 31.82 (q, C-6/12/14/16).

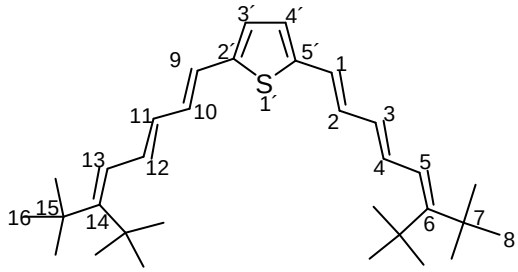
IR (KBr): $\tilde{n}$ = 3442 cm^{-1} (thiophene, b), 3070 (w), 2956 (s), 1740 (w), 1629 (C=C, w), 1481 (m), 1366 (m), 1214 (m), 964 (m), 784 (m).

MS (70 eV): *m*/*z* (%) = 412 [M^+] (100), 355 [M^+-$C(CH_3)_3$] (65), 298 (39), 283 (39), 270 (24), 189 (10), 57 [$C(CH_3)_3$] (40).

UV (CH_3CN): λ_{max} (lg ε) = 236 nm (4.12), 260 (4.20), 266 (4.30), 274 (4.31), 286 (3.93), 376 (4.46), 392 (4.56), 412 (4.43, sh).

Elemental Analysis $C_{28}H_{44}S$ (412.7) Calc. C 81.49% H 10.75% S 7.75%
Found C 80.70% H 10.88% S 7.68%

4.3.66: 2,5-Bis-(6-*tert*-butyl-7,7-dimethyl-octa-1,3,5-trienyl)-thiophene (231)



231

A stirred mixture of 30 mg (0.069 mmol) of **229**, 37 mg (0.153 mmol) of $Na_2S{\cdot}9H_2O$ and 8 mg (0.139 mmol) of KOH in DMSO (20 mL) was heated to 55 °C. The reaction was monitored by TLC and after 5 min, conversion of the starting material to product was complete. The DMSO was removed by vacuum distillation, the remaining precipitate was dissolved by addition of water and the mixture was extracted several times with diethyl ether. The combined organic phases were dried with $MgSO_4$ and the solvent was removed in a rotary evaporator. Purification of the remaining residue by column chromatography on silica gel using ethyl acetate/hexane = 1:10 (v/v) furnished the

thiophene derivative **230** in 100% yield (32 mg, 0.069 mmol) as an orange coloured solid.

R_F (EtOAC/hexane = 1:10): 0.87.

M.p. 188-189 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.32, 1.16 (s, 36H, 8/16/18/20-H), 6.02 (d, 2 H, $^3J_{5\text{-H, 4-H and 13-H, 14-H}}$ = 11.7 Hz, 5/13-H), 6.10 (dd, 2 H, $^3J_{3\text{-H, 4-H and 11-H, 12-H}}$ = 14.3 Hz and $^3J_{3\text{-H, 2-H and 11-H, 10-H}}$ = 10.5 Hz, 3/11-H), 6.49 (d, 2 H, $^3J_{1\text{-H, 2-H and 9-H, 10-H}}$ = 15.0 Hz, 1/9-H), 6.58 (dd, 2 H, $^3J_{2\text{-H, 1-H and 10-H, 9-H}}$ = 15.1 Hz and $^3J_{2\text{-H, 3-H and 10-H, 11-H}}$ = 10.5 Hz, 2/10-H), 6.71 (s, 2 H, 3´/4´-H), 6.84 (dd, 2 H, $^3J_{4\text{-H, 3-H and 12H-11H}}$ = 14.3 Hz and $^3J_{4\text{-H, 5-H and 12-H, 13-H}}$ = 11.7 Hz, 4/12-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 158.11 (s, C-6/14), 142.05 (s, C-2´/5´), 133.21, 131.73, 129.75, 126.56, 124.22, 123.91 (d, C-3´/4´/1/2/3/4/5/9/10/11/12/13), 39.04, 37.99 (s, C-7/15/17/19), 33.81, 31.80 (q, C-8/16/18/20).

IR (KBr): $\tilde{n}$ = 3419 cm^{-1} (thiophene, b), 2959 (s), 1618 (C=C, w), 1459 (w), 1389 (w), 1261 (s), 1217 (m), 1097 (s), 1031 (s), 980 (s), 802 (s).

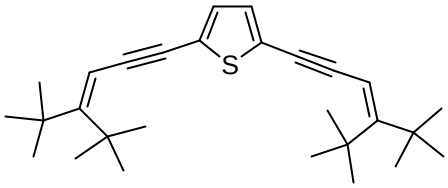
MS (70 eV): *m*/*z* (%) = 464 [M^+] (18), 401 [M^+- $C(CH_3)_3$] (10), 369 (8), 350 (8), 297 (100), 281 (8), 242 (26), 221 (29), 207 (35), 203 (19), 147 (69), 133 (13), 73 (85), 57 [$C(CH_3)_3$] (40).

UV (CH_3CN): λ_{max} (lg ε) = 224 nm (3.49), 272 (4.01), 288 (3.94), 298 (3.99), 310 (4.09), 322 (4.13), 364 (3.74), 406 (4.30), 426 (4.44), 452 (4.34).

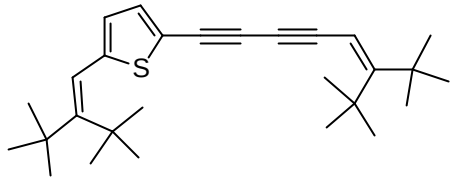
HRMS $C_{32}H_{48}S$ (464.8) Calc. 464.3476

Found 464.3466 ± 2ppm

4.3.67: 2,5-Bis-(4-*tert*-butyl-5,5-dimethyl-hex-3-en-1-ynyl)-thiophene (125) and 2-(2-*tert*-butyl-3,3-dimethyl-but-1-enyl)-5-(6-*tert*-butyl-7,7-dimethyl-oct-5-ene-1,3-diynyl)-thiophene (126)



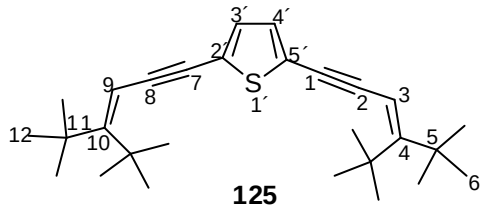
125



126

A mixture of 60 mg (0.021 mmol) of **229**, 225 mg (0.941 mmol) of $Na_2S \cdot 9H_2O$ and 48 mg (0.856 mmol) of KOH in DMSO (50 mL) was stirred for 30 min at 80 °C. The DMSO was removed by vacuum distillation, the remaining precipitate was dissolved by addition of water and the mixture was extracted several times with diethyl ether. The combined organic phases were dried with $MgSO_4$ and the solvent was removed in a rotary evaporator. Purification of the remaining residue on silica gel using ethyl acetate/hexane = 1:10 (v/v) furnished 12 mg (0.030 mmol, 14%) **125** and 12 mg (0.030 mmol, 14%) **126** as orange coloured solids.

2,5-Bis-(4-*tert*-butyl-5,5-dimethyl-hex-3-en-1-ynyl)-thiophene (125)



125

R_F (EtOAC/hexane = 1:10): 0.73.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.21, 1.28 (s, 36 H, 6/11/14/16-H), 6.29 (s, 2 H, 3/9-H), 6.72 (s, 2 H, 3´/4´-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 158.66 (s, C-4/10), 151.46 (s, C-1/7), 144.45 (s, C-2´/5´), 142.94 (s, 2/8), 126.61 (d, C-3´/4´), 97.11 (d, C-3), 38.97, 38.78 (s, C-5/11/13/15), 32.26, 31.88 (q, C-6/11/14/16).

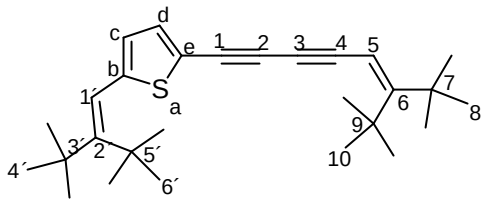
IR (KBr): $\tilde{n}$ = 2960 cm^{-1} (s), 2925 (vs), 2869 (m), 2855 (m), 2038 (C≡C, vw), 1637 (w), 1459 (w), 1261 (m), 1098 (m), 1022 (m), 803 (m).

MS (70 eV): *m*/*z* (%) = 408 [M^+] (100), 393 [M^+-CH_3] (8), 351 [M^+-$C(CH_3)_3$] (40), 337 (12), 295 (40), 279 (10), 267 (12), 202 (7), 57 [$C(CH_3)_3$] (30).

UV ($CHCl_3$): λ_{max} (lg ε) = 242 nm (3.60), 288 (3.74), 370 (3.60), 416 (3.63), 448 (3.58).

Due to the very small quantity of the substance no elemental analysis could be obtained.

2-(2-*tert*-butyl-3,3-dimethyl-but-1-enyl)-5-(6-*tert*-butyl-7,7-dimethyl-oct-5-ene-1,3-diynyl)-thiophene (126)



126

R_F (EtOAc/hexane = 1:10): 0.85.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.16, 1.22, 1.29, 1.39 (s, 36 H, 4´/6´/8/10-H), 5.77 (s, 1 H, 5-H), 6.27 (d, 1 H, $J_{1´\text{-H, c-H}}$ = 0.5 Hz, 1´-H), 6.75 (dd, 1 H, $^3J_{\text{c-H, d-H}}$ = 3.8 Hz, $J_{\text{c-H, 1´-H}}$ = 0.5 Hz, c-H), 6.89 (d, 1 H, $^3J_{\text{d-H, c-H}}$ = 3.8 Hz, d-H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.00 (s, C-6), 159.78 (s, C-2´), 151.91 (s, C-2), 145.44 (s, C-b), 144.16 (s, C-1), 131.20 (d, C-c), 125.33 (d, C-d), 123.67 (s, C-e), 103.68 (d, C-5), 96.26 (d, C-1´), 95.46 (s, C-3), 91.38 (s, C-4), 39.37, 39.11, 38.86, 38.77 (s, C-3´/5´/7/9), 32.17, 31.35 (q, C-8/10), 32.11, 31.87 (C-4´/6´).

IR (KBr): $\tilde{n}$ = 2996 cm^{-1} (s), 2961 (m), 2923 (m), 2180 (C≡C, m), 1636 (m), 1630 (m), 1560 (w), 1484 (m), 1261 (s), 1096 (s), 1049 (s), 803 (s), 792 (s).

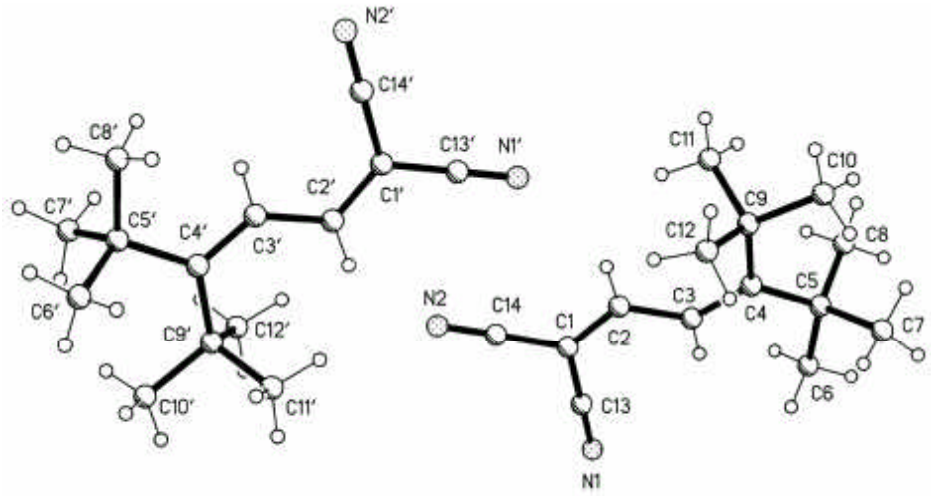
MS (70 eV): *m*/*z* (%) = 408 [M^+] (100), 393 [M^+-CH_3] (12), 351 [M^+-$C(CH_3)_3$] (100), 295 (9), 279 (19), 267 (6), 111 (7), 97 (8), 57 [$C(CH_3)_3$] (24).

UV ($CHCl_3$): λ_{max} (lg ε) = 234 nm (3.70), 274 (3.76), 322 (3.47), 344 (3.72), 366 (4.01), 386 (4.14), 400 (4.10).

Due to the very small quantity of the substance no elemental analysis could be obtained.

5. Single crystal X-ray structure data

5.1. 2-(3-*tert*-Butyl-4,4-dimethyl-pent-2-enylidene)-malononitrile (159)



Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 1510.2 (2) pm	α = 90 °
	b = 1850.1 (3) pm	β = 98.40 (2) °
	c = 986.1 (2) pm	γ = 90 °
Volume, Z	2.7256 (8) nm^3, 8	

Bond lengths [pm]

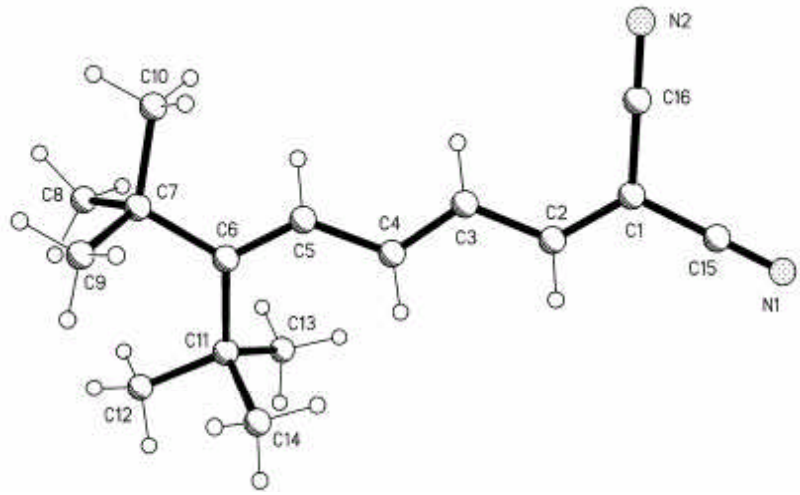
N(1) – C (13)	114.4 (4)	N(2) – C (14)	114.3 (3)
C (1) – C (2)	134.7 (4)	C (1) – C (13)	142.8 (4)
C (1) – C (14)	143.2 (4)	C (2) – C (3)	143.3 (4)
C (3) – C (4)	135.5 (4)	C (4) – C (9)	154.7 (4)
C (4) – C (5)	155.1 (4)	C (5) – C (7)	153.2 (4)
C (5) – C (8)	153.5 (4)	C (5) – C (6)	154.3 (4)
C (9) – C (11)	153.7 (4)	C (9) – C (12)	153.7 (4)
C (9) – C (10)	153.9 (4)	N (1´) – C (13´)	114.6 (3)
N (2´) – C (14´)	114.4 (4)	C (1´) – C (2´)	134.9 (4)

C (1´) – C (14´)	143.2 (4)	C (1´) – C (13´)	143.4 (4)
C (2´) – C (3´)	143.4 (4)	C (3´) – C (4´)	135.2 (4)
C (4´) – C (5´)	154.1 (4)	C (4´) – C (9´)	155.6 (4)
C (5´) – C (6´)	153.1 (4)	C (5´) – C (8´)	153.9 (4)
C (5´) – C (7´)	154.4 (4)	C (9´) – C (12´)	152.6 (4)
C (9´) – C (11´)	153.2 (4)	C (9´) – C (10´)	154.0 (4)

Bond Angles [°]

C(2) – C(1) – C(13)	122.3 (3)	C(2) – C(1) – C(14)	121.8 (3)
C(13) – C(1) – C(14)	115.9 (2)	C(1) – C(2) – C(3)	123.2 (3)
C(4) – C(3) – C(2)	130.1 (3)	C(3) – C(4) – C(9)	120.5 (2)
C(3) – C(4) – C(5)	116.9 (2)	C(9) – C(4) – C(5)	122.4 (2)
C(7) – C(5) – C(8)	110.4 (3)	C(7) – C(5) – C(6)	105.5 (3)
C(8) – C(5) – C(6)	106.2 (3)	C(7) – C(5) – C(4)	113.2 (3)
C(8) – C(5) – C(4)	109.4 (2)	C(6) – C(5) – C(4)	112.0 (2)
C(11) – C(9) – C(12)	111.0 (2)	C(11) – C(9) – C(10)	106.3 (2)
C(12) – C(9) – C(10)	103.5 (2)	C(11) – C(9) – C(4)	108.5 (2)
C(12) – C(9) – C(4)	110.5 (2)	C(10) – C(9) – C(14)	116.9 (2)
N(1) – C(13) – C(1)	179.1 (3)	N(2) – C(14) – C(1)	178.4 (4)
C(2´) – C(1´) – C(14´)	122.7 (2)	C(2´) – C(1´) – C(13´)	122.0 (2)
C(14´) – C(1) – C(13´)	115.2 (2)	C(1´) – C(2´) – C(3´)	122.6 (3)
C(4´) – C(3´) – C(2´)	131.5 (3)	C(3´) – C(4´) – C(5´)	116.8 (2)
C(3´) – C(4´) – C(9´)	120.5 (2)	C(5´) – C(4´) – C(9´)	122.7 (2)
C(6´) – C(5´) – C(8´)	105.1 (2)	C(6´) – C(5´) – C(4´)	112.1 (3)
C(8´) – C(5´) – C(4´)	112.7 (2)	C(6´) – C(5´) – C(7´)	111.4 (3)
C(8´) – C(5´) – C(7´)	105.6 (3)	C(4´) – C(5´) – C(7´)	109.6 (2)
C(12´) – C(9´) – C(11´)	110.8 (2)	C(12´) – C(9´) – C(10´)	105.7 (3)
C(11´) – C(9´) – C(10´)	104.7 (3)	C(12´) – C(9´) – C(4´)	108.5 (2)
C(11´) – C(9´) – C(4´)	109.8 (2)	C(10´) – C(9´) – C(4´)	117.4 (2)
N(1´) – C(13´) – C(1´)	177.7 (3)	N(2´) – C(14´) – C(1´)	179.7 (4)

5.2. 2-(5-*tert*-Butyl-6,6-dimethyl-hepta-2,4-dienylidene)-malononitrile (160)



Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 1532.5 (3) pm	α = 90 °
	b = 677.2 (2) pm	β = 114.336 (10) °
	c = 1572.1 (3) pm	γ = 90 °
Volume, Z	1.4865 (6) nm^3, 4	

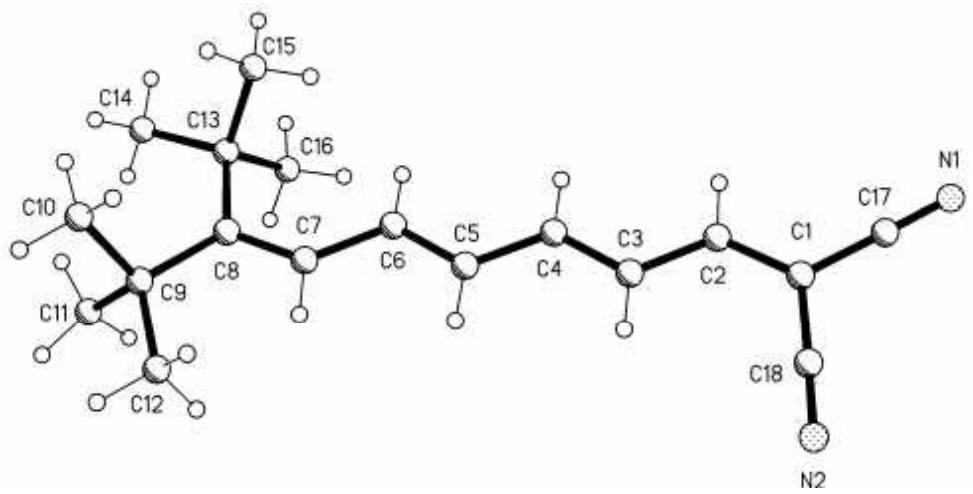
Bond lengths [pm]

C (1) – C (2)	135.3 (3)	C (1) – C (16)	144.2 (4)
C (1) – C (15)	144.3 (3)	C (2) – C (3)	142.2 (4)
C (3) – C (4)	135.4 (3)	C (4) – C (5)	143.8 (3)
C (5) – C (6)	135.5 (3)	C (6) – C (7)	154.9 (3)
C (6) – C (11)	155.4 (3)	C (7) – C (8)	153.7 (4)
C (7) – C (9)	154.3 (4)	C (7) – C (10)	154.5 (3)
C (11) – C (14)	153.6 (4)	C (11) – C (12)	154.1 (3)
C (11) – C (13)	154.2 (4)	C (15) – N (1)	114.0 (3)
C (16) – N (2)	114.6 (3)		

Bond Angles [°]

C(2) – C(1) – C(16)	122.6 (2)	C(2) – C(1) – C(15)	121.9 (2)
C(16) – C(1) – C(15)	115.5 (2)	C(1) – C(2) – C(3)	126.1 (2)
C(4) – C(3) – C(2)	121.6 (2)	C(3) – C(4) – C(5)	122.8 (2)
C(6) – C(4) – C(5)	130.9 (2)	C(5) – C(6) – C(7)	117.6 (2)
C(5) – C(6) – C(11)	120.5 (2)	C(7) – C(6) – C(11)	121.73 (18)
C(8) – C(7) – C(9)	111.0 (2)	C(8) – C(7) – C(10)	105.1 (2)
C(9) – C(7) – C(10)	105.9 (2)	C(8) – C(7) – C(6)	113.4 (2)
C(9) – C(7) – C(6)	108.7 (2)	C(10) – C(7) – C(6)	112.49 (19)
C(14) – C(11) – C(12)	105.2 (2)	C(14) – C(11) – C(13)	111.70 (19)
C(12) – C(11) – C(13)	103.8 (2)	C(14) – C(11) – C(6)	108.8 (2)
C(12) – C(11) – C(6)	117.96 (19)	C(13) – C(11) – C(6)	109.2 (2)
N(1) – C(15) – C(1)	179.4 (3)	N(2) – C(16) – C(1)	179.6 (3)

5.3. 2-(7-*tert*-Butyl-8,8-dimethyl-nona-2,4,6-trienylidene)-malononitrile (161)



Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 1605.9 (3) pm	α = 90 °
	b = 672.40 (8) pm	β = 104.79 (3) °
	c = 1612.8 (2) pm	γ = 90 °

Volume, Z 1.6838 (4) nm^3, 4

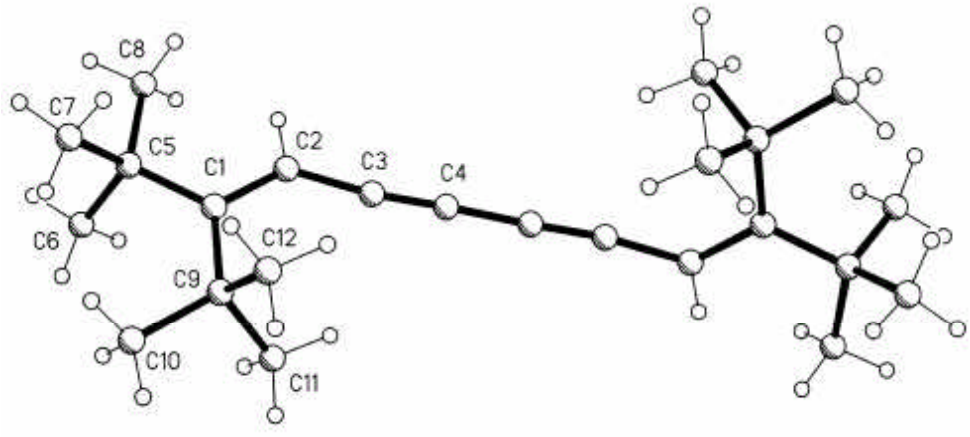
Bond lengths [pm]

N (1) – C (17)	114.2 (2)	N (2) – C (18)	114.5 (2)
C (1) – C (2)	136.6 (2)	C (1) – C (17)	143.0 (2)
C (1) – C (18)	143.8 (2)	C (2) – C (3)	140.6 (2)
C (3) – C (4)	136.0 (2)	C (4) – C (5)	141.2 (2)
C (5) – C (6)	135.7 (2)	C (6) – C (7)	143.6 (2)
C (7) – C (8)	135.6 (3)	C (8) – C (9)	153.8 (2)
C (8) – C (13)	156.0 (2)	C (9) – C (11)	154.1 (2)
C (9) – C (10)	154.3 (2)	C (9) – C (12)	155.0 (2)
C (13) – C (16)	153.4 (2)	C (13) – C (15)	153.7 (2)
C (13) – C (14)	154.3 (2)		

Bond Angles [°]

C(2) – C(1) – C(17)	121.15 (15)	C(2) – C(1) – C(18)	121.76 (14)
C(17) – C(1) – C(18)	117.09 (14)	C(1) – C(2) – C(3)	126.16 (14)
C(4) – C(3) – C(2)	122.53 (14)	C(3) – C(4) – C(5)	124.49 (14)
C(6) – C(5) – C(4)	124.13 (14)	C(5) – C(6) – C(7)	121.70 (14)
C(8) – C(7) – C(6)	132.12 (14)	C(7) – C(8) – C(9)	117.16 (14)
C(7) – C(8) – C(13)	120.54 (13)	C(9) – C(8) – C(13)	122.18 (13)
C(8) – C(9) – C(11)	113.38 (14)	C(8) – C(9) – C(10)	108.76 (14)
C(11) – C(9) – C(10)	110.79 (15)	C(8) – C(9) – C(12)	112.27 (13)
C(11) – C(9) – C(12)	105.54 (14)	C(10) – C(9) – C(12)	105.83 (15)
C(16) – C(13) – C(15)	110.73 (13)	C(16) – C(13) – C(14)	104.32 (14)
C(15) – C(13) – C(14)	105.49 (14)	C(16) – C(13) – C(8)	109.47 (14)
C(15) – C(13) – C(8)	108.61 (14)	C(14) – C(13) – C(8)	118.07 (13)
N(1) – C(17) – C(1)	178.8 (2)	N(2) – C(18) – C(1)	179.19 (18)

5.4. 3,10-Di-*tert*-butyl-2,2,11,11-tetramethyl-dodeca-3,9-diene-5,7-diyne (227)



Crystal system	monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 1533.9 (2) pm	α = 90 °
	b = 615.71 (10) pm	β = 105.328 (6) °
	c = 2348.3 (3) pm	γ = 90 °
Volume, Z	2.1388 (6) nm^3, 4	

Bond lengths [pm]

C (1) – C (2)	135.44 (15)	C (1) – C (5)	154.34 (15)
C (1) – C (9)	155.19 (16)	C (2) – C (3)	142.30 (16)
C (3) – C (4)	120.59 (17)	C (4) – C (4) #1	137.3 (2)
C (5) – C (7)	153.52 (18)	C (5) – C (8)	153.54 (18)
C (5) – C (6)	153.74 (18)	C (9) – C (11)	153.58 (17)
C (9) – C (12)	153.59 (18)	C (9) – C (10)	154.33 (17)

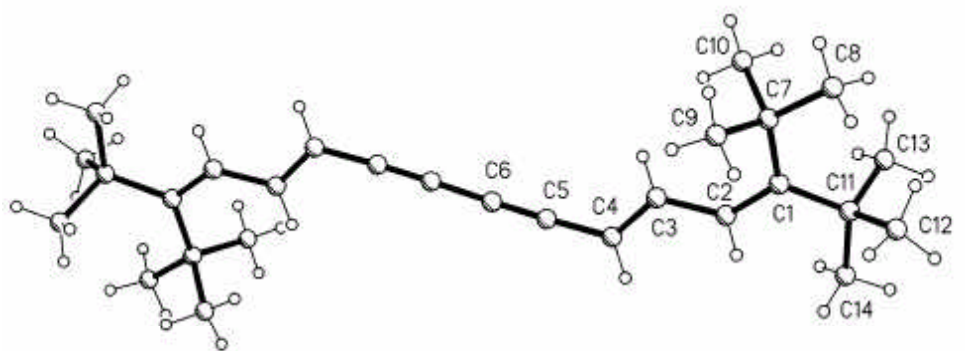
Bond Angles [°]

C(2) – C(1) – C(5)	117.50 (10)	C(2) – C(1) – C(9)	119.04 (10)
C(5) – C(1) – C(9)	123.46 (9)	C(1) – C(2) – C(3)	129.25 (11)
C(4) – C(3) – C(2)	172.95 (13)	C(3) – C(4) – C(4) #1	177.56 (13)

C(7) – C(5) – C(8)	105.73 (12)	C(7) - C (5) – C (6)	110.37 (11)
C(8) – C(5) – C(6)	105.82 (12)	C(7) – C(5) – C(1)	111.88 (10)
C(8) – C(5) – C(1)	112.25 (9)	C(6) – C(5) – C(1)	110.52 (10)
C(11) – C(9) – C(12)	110.02 (10)	C(11) – C(9) – C(10)	104.94 (10)
C(12) – C(9) – C(10)	106.33 (11)	C(11) – C(9) – C(1)	109.65 (10)
C(12) – C(9) – C(1)	108.35 (10)	C(10) – C(9) – C(1)	117.37 (10)

Symmetry transformation used to generate equivalent atoms: #1 -x + 21, -y, -z +1/2.

5.5. 3,14-Di-*tert*-butyl-2,2,15,15-tetramethyl-hexadeca-3,5,11,13-tetraene-7,9-diyne (228)



Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 1164.5 (2) pm	α = 90 °
	b = 796.68 (15) pm	β = 106.559 (10) °
	c = 1357.2 (3) pm	γ = 90 °
Volume, Z	1.2069 (4) nm^3, 4	

Bond lengths [pm]

C (1) – C (2)	135.49 (18)	C (1) – C (11)	154.89 (18)
C (1) – C (7)	155.96 (19)	C (2) – C (3)	145.17 (18)
C (3) – C (4)	134.41 (19)	C (4) – C (5)	141.85 (19)
C (5) – C (6)	120.91 (19)	C (6) – C (6) #1	136.8 (3)

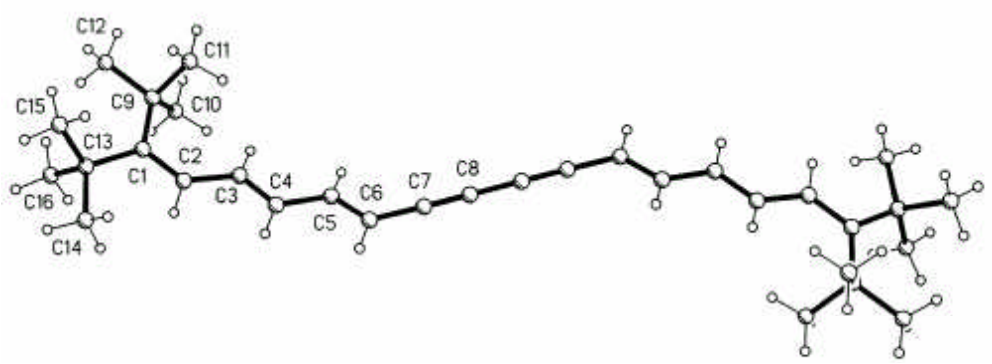
C (7) – C (8)	154.37 (19)	C (7) – C (10)	154.5 (2)
C (7) – C (9)	154.6 (2)	C (11) – C (14)	153.8 (2)
C (11) – C (13)	154.5 (2)	C (11) – C (12)	155.01 (19)

Bond Angles [°]

C(2) – C(1) – C(11)	117.95 (11)	C(2) – C(1) – C(7)	119.60 (11)
C(11) – C(1) – C(7)	122.41 (11)	C(1) – C(2) – C(3)	130.95 (12)
C(4) – C(3) – C(2)	122.90 (13)	C(3) – C(4) – C(5)	122.87 (13)
C(6) – C(5) – C(4)	177.96 (14)	C(5) - C(6) – C(6) #1	178.8 (2)
C(8) – C(7) – C(10)	105.47 (11)	C(8) – C(7) – C(9)	103.51 (11)
C(10) – C(7) – C(9)	111.51 (12)	C(8) – C(7) – C(1)	117.52 (11)
C(10) – C(7) – C(1)	109.44 (11)	C(9) – C(7) – C(1)	109.26 (11)
C(14) – C(11) – C(13)	106.09 (12)	C(14) – C(11) – C(1)	112.47 (11)
C(13) – C(11) – C(1)	109.22 (11)	C(14) – C(11) – C(12)	105.33 (11)
C(13) – C(11) – C(12)	109.97 (11)	C(1) – C(11) – C(12)	113.47 (11)

Symmetry transformation used to generate equivalent atoms: #1 -x + 1, -y, -z +1.

5.6. 3,18-Di-*tert*-butyl-2,2,19,19-tetramethyl-icosa-3,5,7,13,15,17-hexaene-9,11-diyne (229)



Crystal system	monoclinic	
Space group	Pi	
Unit cell dimensions	a = 606.30 (8) pm	α = 75.944 (8) °
	b = 814.08 (12) pm	β = 79.759 (10) °
	c = 1562.3 (2) pm	γ = 71.949 (10) °
Volume, Z	0.70678 (17) nm^3, 1	

Bond lengths [pm]

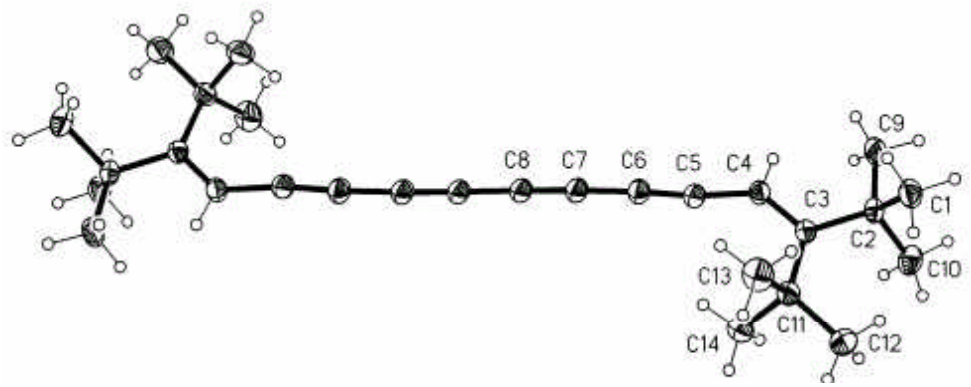
C (1) – C (2)	135.1 (2)	C (1) – C (13)	154.8 (2)
C (1) – C (9)	155.5 (2)	C (2) – C (3)	145.7 (2)
C (3) – C (4)	134. 1 (2)	C (4) – C (5)	143.3 (2)
C (5) – C (6)	133.7 (2)	C (6) – C (7)	141.5 (3)
C (7) – C (8)	120.8 (2)	C (8) – C (8) #1	136.9 (4)
C (9) – C (11)	154.0 (2)	C (9) – C (10)	154.0 (2)
C (9) – C (12)	154.4 (2)	C (13) – C (16)	153.4 (3)
C (13) – C (15)	153.5 (2)	C (13) – C (14)	153.6 (3)

Bond Angles [°]

C(2) – C(1) – C(13)	117.59 (14)	C(2) – C(1) – C(9)	120.26 (14)
C(13) – C(1) – C(9)	122.13 (13)	C(1) – C(2) – C(3)	132.11 (16)
C(4) – C(3) – C(2)	123.24 (16)	C(3) – C(4) – C(5)	124.13 (16)
C(6) – C(5) – C(4)	124.59 (17)	C(5) - C(6) – C(7)	125.21 (18)
C(8) – C(7) – C(6)	176.5 (2)	C(7) – C(8) – C(8) #1	179.2 (3)
C(11) – C(9) – C(10)	110.85 (14)	C(11) – C(9) – C(12)	104.21 (14)
C(10) – C(9) – C(12)	104.58 (14)	C(11) – C(9) – C(1)	109.15 (13)
C(10) – C(9) – C(1)	109.64 (13)	C(12) – C(9) – C(1)	118.20 (13)
C(16) – C(13) – C(15)	110.67 (17)	C(16) – C(13) – C(14)	106.41 (17)
C(15) – C(13) – C(14)	104.08 (15)	C(16) – C(13) – C(1)	111.39 (15)
C(15) – C(13) – C(1)	111.27 (14)	C(14) – C(13) – C(1)	112.70 (14)

Symmetry transformation used to generate equivalent atoms: #1 -x, -y, -z +1

5.7. 3,14-Di-*tert*-butyl-2,2,15,15-tetramethyl-hexadeca-3,13-diene-5,7,9,11-tetrayne (122)



Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.4627 (14) Å	α = 90 °
	b = 8.1292 (10) Å	β = 107.906 (3) °
	c = 13.4476 (18) Å	γ = 90 °
Volume, Z	1192.4 (3) $Å^3$	

Bond lengths [Å]

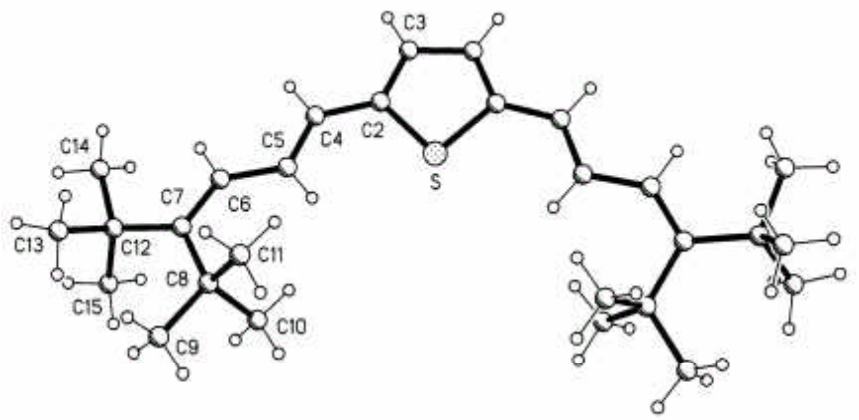
C (1) – C (2)	1.5431 (13)	C (5) – C (6)	1.2132 (13)
C (2) – C (9)	1.5372 (14)	C (6) – C (7)	1.3621 (13)
C (2) – C (10)	1.5441 (14)	C (7) – C (8)	1.2149 (14)
C (2) – C (3)	1.5467 (13)	C (8) – C (8) #1	1.3552 (19)
C (3) – C (4)	1.3564 (13)	C (11) – C (13)	1.5380 (15)
C (3) – C (11)	1.5506 (13)	C (11) – C (14)	1.5424 (15)
C (4) – C (5)	1.4188 (13)	C (11) – C (12)	1.5427 (14)

Bond Angles [°]

C(9) – C(2) – C(1)	106.19 (8)	C(6) – C(5) – C(4)	172.72 (10)
C(9) – C(2) – C(10)	105.73 (8)	C(5) – C(6) – C(7)	175.46 (11)
C(1) – C(2) – C(10)	110.17 (8)	C(8) – C(7) – C(6)	177.35 (11)
C(9) – C(2) – C(3)	112.32 (8)	C(7) - C(8) – C(8) #1	178.91 (15)
C(1) – C(2) – C(3)	109.67 (8)	C(13) – C(11) – C(14)	109.92 (9)
C(10) – C(2) – C(3)	112.51 (8)	C(13) – C(11) – C(12)	107.11 (9)
C(4) – C(3) – C(2)	117.14 (8)	C(14) – C(11) – C(12)	104.35 (9)
C(4) – C(3) – C(11)	119.31 (8)	C(13) – C(11) – C(3)	108.44 (8)
C(2) – C(3) – C(11)	123.43 (8)	C(14) – C(11) – C(3)	109.45 (8)
C(3) – C(4) – C(5)	129.41 (9)	C(12) – C(11) – C(3)	117.39 (8)

Symmetry transformation used to generate equivalent atoms: #1 -x + 1, -y, -z.

5.8. 2,5-Bis-(4-*tert*-butyl-5,5-dimethyl-hexa-1,3-dienyl)-thiophene (230)



Crystal system	tetragonal	
Space group	$I4_1/acd$	
Unit cell dimensions	a = 2275.79 (16) pm	α = 90 °
	b = 2275.79 (16) pm	α = 90 °
	c = 1965.08 (18) pm	γ = 90 °
Volume, Z	10.1776 (14) nm^3,	

Bond lengths [pm]

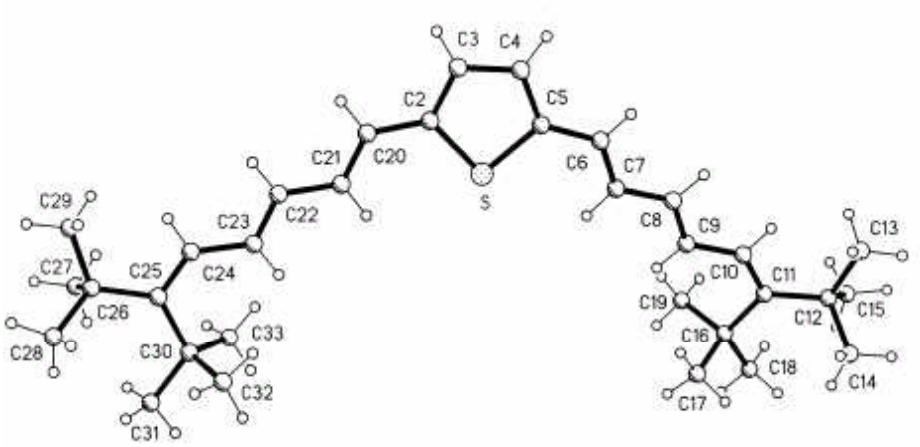
S – C (2)	173.74 (14)	C (2) – C (3)	137.11 (19)
C (2) – C (4)	144.65 (19)	C (3) – C (3) #1	141.0 (3)
C (4) – C (5)	134.3 (2)	C (5) – C (6)	145.48 (19)
C (6) – C (7)	135.2 (2)	C (7) – C (12)	155.07 (19)
C (7) – C (8)	155.8 (2)	C (8) – C (10)	154.5 (2)
C (8) – C (9)	154.8 (2)	C (8) – C (11)	154.8 (2)
C (12) – C (14)	154.2 (2)	C (12) – C (15)	154.72 (19)
C (12) – C (13)	154.82 (19)		

Bond Angles [°]

C(2) #1 – S – C(2)	92.50 (9)	C(3) – C(2) – C(4)	127.85 (13)
C(3) – C(2) – S	110.09 (10)	C(4) – C(2) – S	122.06 (10)
C(2) – C(3) – C(3) #1	113.66 (8)	C(5) – C(4) – C(2)	126.03 (13)
C(4) – C(5) – C(6)	122.82 (13)	C(7) - C(6) – C(5)	131.52 (13)
C(6) – C(7) – C(12)	117.60 (12)	C(6) – C(7) – C(8)	120.03 (12)
C(12) – C(7) – C(8)	122.18 (12)	C(10) – C(8) – C(9)	105.48 (12)
C(10) – C(8) – C(11)	111.37 (12)	C(9) – C(8) – C(11)	103.07 (12)
C(10) – C(8) – C(7)	108.56 (12)	C(9) – C(8) – C(7)	118.03 (12)
C(11) – C(8) – C(7)	110.18 (11)	C(14) – C(12) – C(15)	105.93 (12)
C(14) – C(12) – C(13)	104.92 (12)	C(15) – C(12) – C(13)	110.81 (12)
C(14) – C(12) – C(7)	112.90 (12)	C(15) – C(12) – C(7)	109.36 (11)
C(13) – C(12) – C(7)	112.66 (12)		

Symmetry transformation used to generate equivalent atoms: #1 y + 3 / 4, x – 3 / 4, -z + 5 / 4

5.9. 2,5-Bis-(6-tert-butyl-7,7-dimethyl-octa-1,3,5-trienyl)-thiophene (231)



Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 1164.8 (5) pm	α = 90 °
	b = 3391.7 (6) pm	α = 109.08 °
	c = 820.2 (4) pm	γ = 90 °
Volume, Z	3.0623 (18) nm^3, 4	

Bond lengths [pm]

S – C (2)	173.8 (2)	S – C (5)	174.1 (2)
C (2) – C (3)	136.7 (3)	C (2) – C (20)	143.3 (3)
C (3) – C (4)	140.3 (3)	C (4) – C (5)	136.6 (3)
C (5) – C (6)	143.7 (3)	C (6) – C (7)	134.0 (3)
C (7) – C (8)	143.2 (3)	C (8) – C (9)	133.0 (3)
C (9) – C (10)	144.6 (3)	C (10) – C (11)	135.0 (3)
C (11) – C (16)	154.5 (3)	C (11) – C (12)	154.7 (3)
C (12) – C (13)	153.8 (3)	C (12) – C (14)	154.1 (3)
C (12) – C (15)	154.2 (3)	C (16) – C (17)	153.4 (3)
C (16) – C (19)	154.3 (3)	C (16) – C (18)	155.7 (3)
C (20) – C (21)	133.7 (3)	C (21) – C (22)	143.4 (3)

C (22) – C (23)	134.0 (3)	C (23) – C (24)	144.6 (3)
C (24) – C (25)	135.3 (3)	C (25) – C (26)	155.1 (3)
C (25) – C (30)	155.4 (3)	C (26) – C (29)	153.7 (3)
C (26) – C (28)	154.5 (3)	C (26) – C (27)	154.8 (3)
C (30) – C (33)	153.3 (3)	C (30) – C (31)	154.1 (3)
C (30) – C (32)	154.2 (3)		

Bond Angles [°]

C(2)– S – C(5)	92.52 (10)	C(3) – C(2) – C(20)	127.90 (19)
C(3) – C(2) – S	109.84 (15)	C(20) – C(2) – S	122.26 (16)
C(2) – C(3) – C(4)	113.89 (19)	C(5) – C(4) – C(3)	114.04 (19)
C(4) – C(5) – C(6)	127.85 (19)	C(4) - C(5) – S	109.69 (15)
C(6) – C(5) – S	122.43 (16)	C(7) – C(6) – C(5)	126.4 (2)
C(6) – C(7) – C(8)	125.3 (2)	C(9) – C(8) – C(7)	125.4 (2)
C(8) – C(9) – C(10)	123.5 (2)	C(11) – C(10) – C(9)	133.0 (2)
C(10) – C(11) – C(16)	119.64 (19)	C(10) – C(11) – C(12)	117.62 (19)
C(16) – C(11) – C(12)	122.60 (18)	C(13) – C(12) – C(14)	105.3 (2)
C(13) – C(12) – C(15)	105.4 (2)	C(14) – C(12) – C(15)	110.0 (2)
C(13) – C(12) – C(11)	112.66 (18)	C(14) – C(12) – C(11)	108.95 (19)
C(15) – C(12) – C(11)	114.17 (19)	C(17) – C(16) – C(19)	110.7 (2)
C(17) – C(16) – C(11)	110.0 (2)	C(19) – C(16) – C(11)	109.93 (19)
C(17) – C(16) – C(18)	105.5 (2)	C(19) – C(16) – C(18)	103.0 (2)
C(11) – C(16) – C(18)	117.5 (2)	C(21) – C(20) – C(2)	127.4 (2)
C(20) – C(21) – C(22)	125.3 (2)	C(23) – C(22) – C(21)	125.1 (2)
C(22) – C(23) – C(24)	123.1 (2)	C(25) – C(24) – C(23)	132.7 (2)
C(24) – C(25) – C(26)	117.8 (2)	C(24) – C(25) – C(30)	119.42 (19)
C(26) – C(25) – C(30)	122.82 (19)	C(29) – C(26) – C(28)	105.7 (2)
C(29) – C(26) – C(27)	105.7 (2)	C(28) – C(26) – C(27)	110.2 (2)
C(29) – C(26) – C(25)	112.44 (19)	C(28) – C(26) – C(25)	112.1 (2)
C(27) – C(26) – C(25)	110.37 (19)	C(33) – C(30) – C(31)	105.5 (2)

C(33) – C(30) – C(32)	111.6 (2)	C(31) – C(30) – C(32)	103.2 (2)
C(33) – C(30) – C(25)	109.76 (19)	C(31) – C(30) – C(25)	117.7 (2)
C(32) – C(30) – C(25)	108.92 (18)		

References:

1. F. Bohlmann, T. Burkhardt, C. Zdero, *Naturally Occuring Acetylenes*, Academic Press, London, **1973**.
2. H. Hopf, *Classics in Hydrocarbon Chemistry*, Wiley-VCH, Weinheim, **2000**.
3. O. Isler, *Carotenoids*, Birkhäuser Verlag, Basel, **1971**.
4. P. Karrer, C. H. Eugster, *Helv. Chim. Acta*, **1950**, *33*, 1172 - 1174.
5. F. Zeng, E. Negishi, *Organic Letters*, **2001**, *3*, 719 - 722.
6. The Royal Swedish Academy of Sciences awarded the *Nobel Prize in Chemistry for* **2000** to A. J. Heeger, A. G. MacDiarmid, H. Shirakawa "for the discovery and development of electrically conductive polymers".
7. L. F. Trüb, *Naturwissenschaftliche Rundschau*, **2000**, *53*, 98 - 99.
8. D. L. Pearson, J. M. Tour, *J. Org. Chem.*, **1997**, *62*, 1376 – 1378.
9. R. Kuhn, *Angew. Chem.*, **1937**, *50*, 703 - 718.
10. F. Sondheimer, D. A. Ben-Efraim, R. Wolovsky, *J. Am. Chem. Soc.*, **1961**, *83*, 1675 - 1681; *cf*. F. Sondheimer, D. A. Ben-Efraim, Y. Gaoni, *J. Am. Chem. Soc.*, **1961**, *83*, 1682 - 1685.
11. P. Nayler, M. C. Whiting, *J. Chem. Soc.*, **1955**, 3037 - 3047.
12. G. Wittig, G. Geissler, *Justus Liebigs Ann. Chem.*, **1953**, *580*, 44 - 57.
13. F. Bohlmann, H. J. Mannhardt, *Chem. Ber.*, **1956**, *89*, 1307 - 1315.
14. A. Kiehl, A. Eberhardt, K. Müllen, *Lieb. Ann. Chem.*, **1995**, 223 - 230.
15. (a) E. Negishi, O. A. King, W. L. Klima, W. Patterson, A. Silveria, *J. Org. Chem.*, **1980**, *4*, 2526 - 2528. (b) E. Negishi, O. A. King, J. M. Tour, *Org. Synth.*, **1985**, *64*, 44 - 47.
16. J. Thiobonnet, A. Abarbri, A. Duchene, J. -L. Parrain, *Synlett*, **1999**, 141 - 143.
17. J. Uenishi, R. Kawahoma, O. Yonemitsu, A. Wada, M. Ito, *Angew. Chem.*, **1998**, *110*, 334 - 336.
18. A. Torrado, B. Iglesias, S. Lopez, A. R. de Lara, *Tetrahedron*, **1995**, *51*, 2435 - 2454.
19. A. Kasatkin, R. J. Whitby, *J. Am. Chem. Soc.*, **1999**, *121*, 7039 - 7049.
20. B. Crousse, M. Alami, G. Linstrumelle, *Tetrahedron*, **1995**, *36*, 4245 - 4248.
21. B. Crousse, M. Mladenova, P. Ducept, M. Alami, G. Linstrumelle, *Tetrahedron*, **1999**, *55*, 4353 - 4368.
22. E. Shirakawa, H. Yoshida, Y. Nakao, T. Hiyama, *J. Am. Chem. Soc.*, **1999**, *121*, 4290 - 4291, and the references herein.
23. (a) H. Hopf, C. Mlynek, D. Klein, *Eur. J. Org.*, **2001** in press. (b) D. Fischer, *Dissertation*, TU Braunschweig, **2000**.
24. R. Eastmond, T. R. Johnson, D. R. M. Walton, *Tetrahedron*, **1972**, *28*, 4601 - 4616.
25. (a) C. Glaser, *Ber. Dtsch. Chem. Ges.*, **1869**, *2*, 422 - 424. (b) C. Glaser, *Ann. Chem. Pharm.*, **1870**, *154*, 137 - 171.
26. A. Baeyer, *Ber. Dtsch. Chem. Ges.*, **1882**, 15, 50 - 56.
27. A. Baeyer, *Ber. Dtsch. Chem. Ges.*, **1885**, 18, 674 - 681.
28. A. S. Hay, *J. Org. Chem.*, **1962**, *27*, 3320 - 3321.
29. M. Yamaguchi, H. -J. Park, M. Hirama, K. Torisu, S. Nakamura, T. Minami, H. Nishihara, T. Hiraoka, *Bull. Chem. Soc. Jpn.*, **1994**, *67*, 1717 - 1725.
30. G. Eglinton, A. R. Galbraith, *Chem. Ind.* (London) **1956**, 737 - 738.
31. E. R. H. Jones, H. H. Lee, M. C. Whiting, *J. Chem. Soc.*, **1960**, 3483 - 3489.

32. F. Bohlmann, *Chem. Ber.*, **1953**, *86*, 657 - 667.
33. T. R. Johnson, D. R. M. Walton, *Tetrahedron*, **1972**, *28*, 5221 - 5236.
34. M. Nakagawa, S. Akiyama, K. Nakasuji, K. Nishimoto, *Tetrahedron*, **1971**, *27*, 5401-5418, and the references herein.
35. F. Toda, Y. Tokumaru, *Chem. Lett.*, **1990**, 987 - 990.
36. K. Sonogashira in *Comprehensive Organic Synthesis*, Vol. 3 (Eds. I. Fleming, B. Trost), Pergamon, New York, **1991**.
37. G. Zehng, W. Lu, J. Cai, *J. Nat. Prod.*, **1999**, *62*, 626 - 628.
38. K. C. Nicolaou, A. L. Smith in *Modern Acetylene Chemistry* (Eds. P. J. Stang, F. Diederich), VCH, Weinheim, **1995**.
39. D. Elbaum, T. B. Nguyen, W. L. Jorgensen, S. L. Schreiber, *Tetrahedron*, **1994**, *50*, 1503 - 1518.
40. For a review see; P. Siemsen, R. C. Livingstone, F. Diedrich, *Angew. Chem.*, **2000**, *112*, 2740 - 2767; *Angew. Chem. Int. Ed. Engl.*, **2000**, *39*, 2632 - 2657, and the references herein.
41. For conductive polymers see; (a) H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, A. J. Heeger, *J. Chem. Soc. Chem. Comm.*, **1977**, 578 - 580. (b) C. K. Chiang, C. R. Fischer, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, A. G. MacDiarmid, *Phys. Rev. Lett.*, **1977**, *39*, 1098. (c) C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, Y. W. Park, H. Shirakawa, *J. Am. Chem. Soc.*, **1978**, *100*, 1013 - 1015. (d) M. G. Kanatzidis, *Chem. Eng. News*, **1990**, *3*, 36.
42. (a) J. M. Tour, M. Kozaki, J. M. Seminario, *J. Am. Chem. Soc.*, **1998**, *120*, 8486 - 8493. (b) V. Alain, L. Thouin, M. B. Desce, U. Gubler, C. Bosshard, P. Günter, J. Müller, A. Fort, M. Barzoukas, *Adv. Mater.* **1999**, *11*, 1210 - 1214. (c) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature*, **1990**, *347*, 539 - 542. (d) R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Lögdlung, W. R. Salaneck, *Nature*, **1999**, *397*, 121 - 128. (e) L. B. Groenendad, F. Jonas, D. Freitag, H. Pielartzik, J. R. Reynolds, *Adv. Mater.* **2000**, *12* (7), 481 - 494. (f) M. Berggren, O. Inganäs, G. Gustafsson, J. C. Gustafsson-Carlberg, J. Rasmusson, M. R. Andersson, T. Hjertberg, O. Wennerström, *Nature*, **1994**, *372*, 444. (g) J. M. Lehn, *Angew. Chem.*, **1988**, *100*, 91 - 116; *Angew. Chem. Int. Ed. Engl.*, **1988**, *27*, 89 - 114. (h) T. Murahashi, E. Mochizuki, Y. Kai, H. Kurosawa, *J. Am. Chem. Soc.*, **1999**, *121*, 10660 - 10661. (i) C. W. Spangler, R. A. Rathunde, *J. Chem. Soc. Chem. Comm.*, **1989**, 26 - 27. (j) M. Maldenova, L. Ventelon, M. B. -Desce, *Tet. Lett.*, **1999**, *40*, 6923 - 6926.
43. H. Ikeda, Y. Kawabe, T. Sakai, K. Kawasaki, *Chem. Lett.*, **1989**, 1285 - 1288.
44. H. Higuchi, M. Kondo, H. Yonehara, J. Ojima, M. Iyoda, *Bull. Chem. Soc. Jpn.*, **1993**, *66*, 275 - 281.
45. H. E. Zimmerman, D. Armesto, M. G. Amezua, T. P. Gannet, R. P. Johnson, *J. Am. Chem. Soc.*, **1979**, *101*, 6367 - 6383.
46. H. Hopf, C. Mlynek, D. Klein, M. Traetteberg, P. Bakken, *Eur. J. Org.*, **2001**, 1385 - 1391.
47. R. W. Murray, *Acc. Chem. Res.* **1980**, *13*, 135 - 141.
48. C. D. Bain, J. Evall, G. M. Whitesides, *J. Am. Chem. Soc.*, **1989**, *111*, 7155 - 7164.

49. R. C. Jagessar, J. M. Tour, *Org. Lett*. **2000**, *2*, 111 - 113.
50. J. Hu, D. L. Mattern, *J. Org. Chem*., **2000**, *65*, 2277 - 2281.
51. J. P. Collman, M. Zhang, S. Stanzo, C. J. Sunderland, A. Aukauloo, K. Berg, L. Zeng, *Synthesis*, **2001**, *No.3*, 367 - 369.
52. P. Barta, J. Birgerson, S. Guo, H. Arwin, W. R. Salaneck, M. Zagorska, *Adv. Mater*., **1997**, *9*, 135 - 143.
53. C. W. Spangler, P. K. Liu, A. A. Dembek, K. O. Havelka, *J. Chem. Soc. Perkin Trans. 1*, **1991**, 799 - 802.
54. P. Blanchard, H. Brisset, A. Riou, R. Hierle, J. Roncali, *J. Org. Chem. Soc.*, **1998**, *63*, 8310 - 8319.
55. For bimolecular nucleophilic substitution with allylic rearrangement see; R. M. Magid, *Tetrahedron*, **1980**, *36*, 1901 - 1930.
56. H. B. Hass, M. L. Bender, *J. Am. Chem. Soc*., **1949**, *71*, 1767 - 1769.
57. N. Krause, *Chem. Ber*., **1991**, 124, 2633 - 2635.
58. J. March, *Advanced Organic Chemistry*, 4th Edition, Wiley, Newyork, **1992**, 959.
59. (a) N. Nakanishi, V. B. N. M Arhaboldi, K. Tsujimoto, B. Honig, *J. Am. Chem. Soc*., **1980**, *102*, 7947 - 7949. (b) K. C. Nicolaou, T. K. Chakraborty, R. A. Daines, N. S. Simpkins, *J. Chem. Soc. Chem. Commun.*, **1986**, 413 - 416. (c) M. Kinoshita, H. Takami, M. Taniguchi, T. Tamari, *Bull. Chem. Soc. Jpn*., **1987**, *60*, 2151 - 2161.
60. O. Bayer in *Methoden der Organischen Chemie* (Ed. E. Müller), Band 7/1, Thieme Verlag, Stuttgart, 4th Auflage, **1973**, 739 - 746.
61. F. S. Prout, *J. Org. Chem*., **1930**, *18*, 928 - 930.
62. D. A. Skoog, J. L. Leary, *Principles of Instrumental Analysis*, Saunders College Publishing, 4th Edition, **1991**, 150 - 156.
63. J. Fabian, H. Hartmann, *Light Absorption of Organic Colorants*, Berlin, **1980**.
64. M. Hesse, H. Maier, B. Zeeh, *Spektroskopische Methoden in der Organischen Chemie*, 4. Auflage, Stuttgart, **1991**.
65. R. M. Silverstein, G. C. Bassler, T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 5th Edition, Wiley, New York, **1991**, 299 - 305.
66. Y. Frukawa in *The chemistry of dienes and polyenes* (Ed. Z. Rappaport), John Wiley and Sons, Chichester, **1997**, 149 - 172.
67. H. Kuhn, *J. Chem. Phys*., **1949**, *17*, 1198 - 1212.
68. (a) S. F. Birch, D. T. McAllan, *J. Chem. Soc*., **1951**, 2556 - 2562. (b) C. G. Moore, B. R. Trego, *Tetrahedron*, **1962**, *18*, 205 - 218.
69. J. Nishio, *J. Chem. Soc. Chem. Commun*., **1989**, 205 - 206.
70. A. Gerdes, *Dissertation*, TU Braunschweig, **1991**.
71. A. Ulmen, C. S. Willand, W. Köhler, D. R. Robello, D. J. Williams, L. Handley, *J. Am. Chem. Soc*., **1990**, *112*, 7083 - 7090.
72. T. Schrader, *Chem. Eur. J*., **1997**, *3*, 1537 - 1541.
73. D. M. Wagner, D. R. Arnold, *Can. J. Chem*., 62, **1984**, 1164 - 1168.
74. T. Itoh, K. Gotoh, N. Ishikawa, T. Hamaguchi, M. Kubo, *J. Org. Chem*., **1996**, *61*, 1867 - 1869.
75. P. Michell, D. Gennet, A. Rassat, *Tetrahedron Lett*., **1999**, 40, 8575 - 8578, *c.f*. P. Michell, A. Rassat, *Tetrahedron Lett*., **1999**, *40*, 8579 - 8581.
76. L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, **1971**.

77. L. Brandsma, H. Hommes, H. D. Verkruijsse, A. J. Kos, W. Neugebauer, W. Baumgärtner, P. von R. Schleyer, *Red. Trav. Chim. Pays-Bas*, **1988**, *107*, 286 - 295.
78. (a) E. McMurry, M. P. Flemming, *J. Am. Chem. Soc.*, **1974**, *96*, 4708 - 4709. (b) T. Mukaiyama, T. Sato, J. Hanna, *Chem. Lett.*, **1973**, 1041 - 1044.
79. (a) A. Krüger, *Dissertation*, TU Braunschweig, **2000**. (b) M. Srinivasan, *Dissertation*, IIT Madras, India, **2001**.
80. S. Kozhushkov, T. Haumann, K. Boese, B. Knierim, S. Scheib, P. Bauerle, A. de Meijere, *Angew. Chem.* **1995**, *107*, 859 - 861; *Angew. Chem. Int. Ed. Engl.*, **1995**, *34*, 781 - 783.
81. For mirror image rule see; J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 2nd Edition, **1999**, 1-20.
82. Z. Meic, T. D. Vikic, H. Dasten, *Org. Magn. Reson.*, **1984**, *22*, 237 - 244.
83. (a) C. K. Bradsher, J. C. Parham, *J. Heterocycl. Chem.*, **1964**, *1*, 30 - 33. (b) B. Gross, *J. Am. Chem. Soc.*, **1968**, *90*, 3120.
84. L. Engman, *J. Org. Chem.*, **1984**, *49*, 3559 - 3563.
85. J. Robert, M. Anouti, G. Bosser, J. L. Parrain, J. Paris, *J. Chem. Soc. Perkin. Trans. 2*, **1995**, 1639 - 1644.

Lebenslauf

Vor- und Zuname:	Pinar Kiliçkiran
Geburtsdatum:	08. Februar 1972
Geburtsort:	Ankara/Türkei
Staatsangehörigkeit:	türkisch
Familienstand:	ledig

Schulbildung

1978 - 1983	Grundschule, "Gazi Osman Pasa Ilkokulu", Ankara/Türkei
1983 - 1990	Gymnasium, "TED Ankara Koleji", Ankara/Türkei

Hochschulbildung

1990 - 1991	Studium der Physik an der Middle East Technical University (M.E.T.U.), Ankara/Türkei
1991 - 1995	Studium der Chemie an der M.E.T.U.
02.08.1995	Bachelor of Science in Chemistry
1995 - 1997	Masterarbeit an der M.E.T.U. unter der Leitung von Prof. Dr. A. S. Demir Thema der Masterarbeit: A novel Method for the Reduction of Carboxylic Acids in the Presence of Heterogeneous Catalysts
19.02.1997	Master of Science in Chemistry
09.1997 - 02.1998	Deutschkurs an der Ruhr Universität Bochum
seit April 1998	Anfertigung der Dissertationsarbeit am Institut für Organische Chemie, TU Braunschweig, unter Anleitung von Prof. Dr. H. Hopf
09.1998 - 03.1999	wissenschaftliche Hilfskraft am Institut für Organische Chemie der TU Braunschweig
04.1999 - 09.2001	Stipendiatin der Hans Böckler Stiftung

Veröffentlichungen

1. F. Gerson, P. Merstetter, D. Fischer, H. Hopf, P. Kilickiran, *Helv. Chim. Acta*, **1999**, *82*, 1266 – 1273.
2. P. Kilickiran, S. Sankararaman, H. Hopf, *Indian J. Chem.*, **2001,** *40B*, 781 – 785.